STUDIES ON THE SOLVENT DEPENDENCE IN THE REACTION OF A FEW (ANTHRACEN-9-YL)METHYLAMINES AND SULFANES WITH REACTIVE ACETYLENES

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DOCTOR OF PHILOSOPHY

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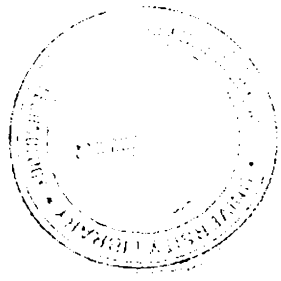

BY

REKHA R. MALLIA

DEPARTMENT OF APPLIED CHEMISTRY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
COCHIN - 682 022

December 2007

CERTIFICATE

This is to certify that the thesis herewith is an authentic record of research work carried out by the author under my supervision, in partial fulfilment of the requirements for the degree of Doctor of Philosophy of Cochin University of Science and Technology, and further that no part thereof has been presented before for any other degree.

Kochi-22
14th December, 2007

Dr. Prathapan S.
(Supervising Guide)
Reader in Organic Chemistry
Department of Applied Chemistry
Cochin University of Science and Technology
Kochi-682 022

DECLARATION

I hereby declare that the work presented in this thesis entitled: **"Studies on the Solvent Dependence in the Reaction of a Few (Anthracen-9-yl)methylamines and Sulfanes with Reactive Acetylenes"** is original and was carried out by me independently under the supervision of Dr. Prathapan S., Reader in Organic Chemistry, Department of Applied Chemistry, Cochin University of Science and Technology, Kochi-682 022, India, and has not been included in any other thesis submitted previously for the award of any other degree.

Rekha R. Mallia

Kochi-22
14th December, 2007

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CONTENTS

Abstract

The thesis entitled **'Studies on the Solvent Dependence in the Reaction of a Few (Anthracen-9-yl)methylamines and Sulfanes with Reactive Acetylenes'** is divided into six chapters. In **Chapter 1** a general survey of electron transfer reactions, Diels-Alder reactions and Michael-type additions is presented. A detailed discussion on the synthesis of several (anthracen-9-yl)methylamines is presented in **Chapter 2**. In **Chapter 3**, results of preliminary photophysical studies on a few (anthracen-9-yl)methylamines are compiled. A detailed discussion on extensive examination of dependence in the reaction of (anthracen-9-yl)methylamines with reactive acetylenes is presented **Chapter 4**. Details on the synthesis and reaction of a few (anthracen-9-yl)methylsulfanes with DMAD are described in **Chapter 5**.

Chapter 1: Electron Transfer Reactions, Diels-Alder Reactions and Michael Type Additions - Précis

Electron transfer process plays a decisive role in several electrochemical, photochemical and biochemical redox reactions. Single electron transfer reactions of amines leads to the formation of radical intermediates that can be used for the synthesis of amino acids, alkaloids, and several other nitrogen-containing compounds of biological and pharmaceutical importance. Amine-arene systems having 'donor-spacer-acceptor' type structural features facilitate intramolecular quenching of excited states by electron transfer. Usually one electron oxidation of amines results in *N*-dealkylation as observed in most thermal, electrochemical and photochemical processes.

Diels-Alder reaction is one of the major synthetic strategies employed to generate cyclic and bicyclic compounds. Its applications lead to significant increase in molecular complexity such as molecular size, topology,

stereochemistry, functionality, and appendages. Michael addition of carbon nucleophiles to electron deficient olefins is a classical and fundamental carbon–carbon bond-forming reaction. This reaction and its close variants have been extensively used in organic synthesis. Addition of nucleophilic species including amines, alcohols and thiols to electron deficient double and triple bonds hold tremendous application potential and utility in organic synthesis. A brief survey of these reactions and their importance emphasising on amines and sulphanes is provided in this chapter.

Chapter 2: Synthesis of (Anthracen-9-yl)methylamines

We synthesised several (anthracen-9-yl)methylamines having a tertiary amine component appended at the 9-position of anthracene *via* a methylene spacer (Chart 1) through the application of Leuckart reaction and nucleophilic substitution reactions. The *N*-substituents were chosen such a way to vary the steric and electronic environment of the donor component.

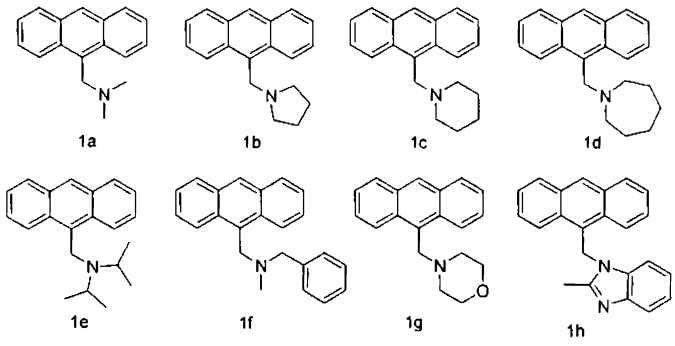


Chart 1

Chapter 3: Preliminary Photophysical Investigations on (Anthracen-9-yl)methylamines

Arene-amines systems are known to undergo interesting photo-initiated electron transfer (PET) in their excited states which leads to quenching of arene fluorescence. We explored the PET quenching process in the

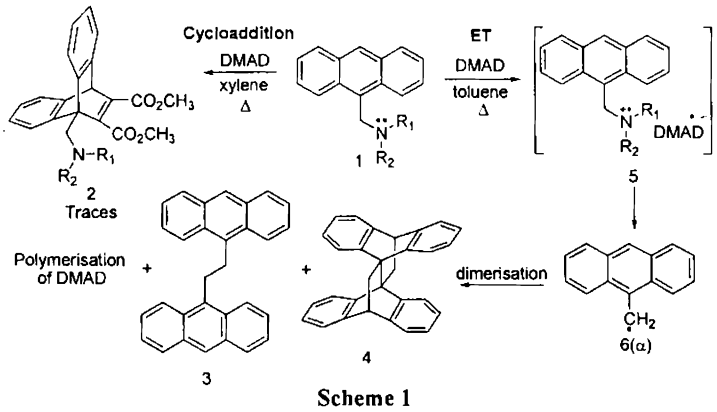
(anthracen-9-yl)methylamines synthesised by us by studying the absorbance spectra, fluorescent emission spectra, the decay kinetics using time correlated single photon counting techniques (TCSPC) and calculated the relative quantum yield, change in free energy and rate constant of photoinitiated electron transfer of **1a-h** in methanol solvent. Based on the results we illustrated the PET behaviour of **1a-h** with respect to 9-methylanthracene.

Chapter 4: Reactions of (Anthracen-9-yl)methylamines with Reactive Acetylenes

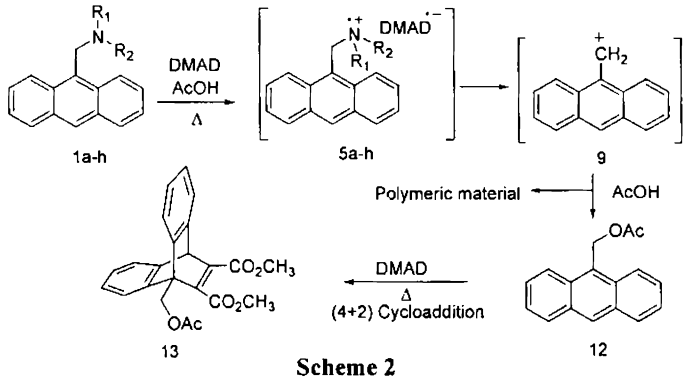
In the reaction between (anthracen-9-yl)methylamines and reactive acetylenes under conditions favourable for Diels-Alder reaction, we encountered novel 'donor-acceptor' type reaction possibilities between the amine and acetylene components. We examined the mechanistic aspects and demonstrated a dramatic solvent dependence of competing electron transfer and nucleophilic addition pathways exhibited by (anthracen-9-yl)methylamines. Reaction of **1a** with DMAD in nonpolar solvents yielded 1,2-bis(9-anthracenyl)ethane (**3**) and lepidopterene (**4**) along with trace amounts of the Diels-Alder adduct **2**. The unusual reaction may be viewed to take place through a single electron-transfer from the tertiary amine to DMAD followed by homolytic cleavage of C-N bond generating the 9-anthracenemethyl radical **6** (Scheme 1). The 9-anthracenemethyl radical thus formed underwent dimerisation, followed by intramolecular Diels-Alder reaction to form lepidopterene.

In reaction of (anthracen-9-yl)methylamines and reactive acetylenes in glacial acetic acid, (anthracen-9-yl)methyl acetate (**12**) and the corresponding barrelene **13** were formed as products. The reaction takes place through the initial transfer of an electron from the amine lone pair to DMAD leading to the weakening and eventual heterolytic cleavage of C-N bond to form 9-

anthracenemethyl cation (**9**), which is captured by acetic acid to give **9** (Scheme 2).

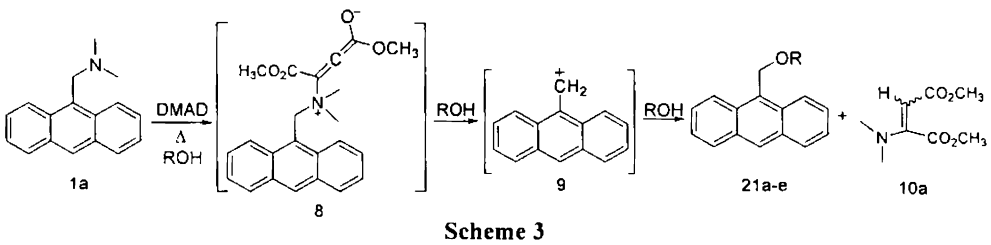


Scheme 1



Scheme 2

When the reaction was carried out in alcohol solvents we obtained corresponding (anthracen-9-yl)methyl ether **21** and the dialkylaminoalkylmaleate/fumarates **10a-h** (Scheme 3). Formation of **10a-h** indicates that nucleophilic addition of the amine component on to DMAD takes place forming a Michael-type adduct/zwitterion **8** leading to a heterolytic cleavage of C-N bond giving rise to dialkylaminoalkylmaleate/fumarates **10** and 9-anthracenemethyl cation **9**, which is captured by the solvent to give **12**. These reactions are quite general and similar results were obtained with all the amine-appended anthracenes examined by us.



Scheme 3

To study the influence of nature of acetylenes on the reaction, we carried out the reactions using different acetylenes and observed that the magnitude of electron deficiency of the acetylene has a definite influence on the efficiency and mechanistic pathways of the reaction.

Chapter 5: Synthesis and Reactions of (Anthracen-9-yl)methylsulphanes with DMAD

As an extension, we explored the mechanistic possibilities of solvent dependent reactions in sulphur analogs: (anthracen-9-yl)methylsulphanes as sulphur compounds are known for radical as well as nucleophilic reactions under thermal and photochemical conditions. We synthesised (anthracen-9-yl)methylsulphanes **2a** and **b** (Chart 2) through nucleophilic substitution of thiols on 9-chloromethylanthracene in presence of a non-nucleophilic base like DBU. (Anthracen-9-yl)methylsulphanes reacted with DMAD in similar profile as that of anthracen-9-yl)methylamines.

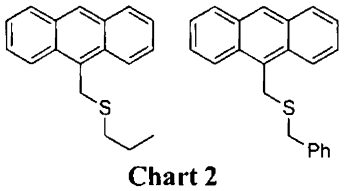


Chart 2

Note: The numbers given to various compounds herein correspond to those given in respective chapters. We have reported only the relevant data for the characterisation of novel compounds synthesised by us.

Chapter – 1

ELECTRON TRANSFER REACTIONS, DIELS-ALDER REACTIONS AND MICHAEL-TYPE ADDITIONS - PRÉCIS

1.1. Abstract

Herein, we present a précis of electron transfer reactions, electron transfer mediated nucleophilic substitution reactions, Diels-Alder reactions and Michael-type addition reactions pertinent to amines and sulphanes, since these form the basis of our proposed investigations. We have also presented a conceptual picture of photoinitiated electron transfer reactions given by amines.

1.2. Electron Transfer Reactions - An Overview

Electron transfer (ET), or the act of moving an electron from one atom to another, is amongst the simplest yet one of the most critical of chemical processes. The process of efficiently and controllably moving electrons is one of the primary regulation mechanisms in chemistry and biology. Without stringent control of electron transfer in living organisms, life could simply not exist. Vital biochemical processes such as photosynthesis and nitrogen fixation are driven by ET processes. It is unsurprising, therefore, that much effort is placed on understanding the fundamental principles that control and define the act of adding and/or removing electrons from chemical species. For a long time, electron pair transfer provided a mechanistic basis for understanding reactivity in organic reactions. As an extreme example, the

reductive hydrodimerisation of activated olefins was thought originally to proceed by which one molecule of substrate extracting a pair of electrons from the electrode leading to a dianion which then add to a second molecule of the substrate in a Michael-type fashion.[1]

It has been established that electron transfers between electrodes and organic molecules are one-electron transfers, even if these primary steps are associated with homogeneous reactions that may be of the Lewis acid-base type.[2] In homogeneous chemistry and also in photochemistry, single-electron transfer has been shown to play an important role. SRN1 substitution reaction in which anion radicals are an essential part of the chain processes and in which single-electron transfer plays an important role in both initiation and termination steps serves as an illustrative example of a single-electron transfer process.[3-9] Even classical electron-pair-transfer reactions such as SN2 substitutions may be viewed in several cases as single-electron-transfer reactions, provided electron transfer is concerted with bond breaking and bond formation.[9]

In chemistry, electron transfer (ET) is a mechanistic description of the thermodynamic concept of redox reactions, wherein the formal oxidation states of both reaction partners change. The Marcus-Hush model[10-12] provided an efficient, though approximate, means of relating structure and reactivity relationships for reactions involving outer-sphere electron transfers, as well as to dissimilative electron transfers, i.e., reactions in which electron transfer is concerted with breaking of one bond. Electron transfer is a rapid process. For an electron transfer reaction to take place, the energy levels of the donor orbitals and the acceptor orbitals must be similar since there is no time for nuclear reorganization which would change the energy level to occur.

In reactions involving electron transfer and bond breaking, the two steps may be concerted or successive. How one can distinguish experimentally between the two mechanisms and what factors control the occurrence of one or the other mechanism are questions that have important implications in all fields of electron-transfer chemistry. The link between electron-transfer and radical chemistry rests on the nature of the bond-breaking mechanism together with the redox properties of the radicals that may be thus generated. In photochemistry, strategies aimed at minimizing or suppressing the effects of back electron transfer are also dependent upon the mechanism of electron transfer-bond breaking reactions.[13]

In stepwise reactions, the anion radical, formed upon initial electron transfer, cleaves in a second step, to the corresponding radical and the anion of the leaving group. The latter step may itself be viewed as a special case of dissociative electron transfer where the unpaired electron located in one portion of the molecule dissociatively reduces a bond belonging to the same molecule. Adapting the intermolecular dissociative-electron transfer reaction model to intramolecular dissociative-electron transfer reactions will at the same time allow one to describe the dynamics of the reverse reaction; and the reaction of a nucleophile with a radical as an associative-single-electron transfer reaction. These two reactions are essential steps of the chain propagation loop in SRN1 substitutions and thus the modelling of their dynamics is an important step in the prediction of the dependency of SRN1 reactivity upon the structures of the substrate and the nucleophile.

1.3. Electron Transfer Mediated Nucleophilic Substitutions

A number of nucleophilic as well as electrophilic reactions are electron transfer processes, in which initial transfer of a single electron occurs followed by a radical mechanism. Nucleophilic substitution reactions are prominent

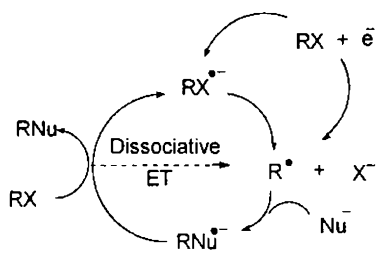
with both aliphatic and aromatic substrates. In aliphatic family, SN1, SN2 and related mechanism involving transfer of a pair of electrons predominates. In the aromatic family, two electron processes such as SNAr, benzyne and halogen-metal exchange mechanisms usually account for nucleophilic substitution reaction. With unsaturated aliphatic compounds, addition reactions are also very common. Most nucleophilic substitution and addition reactions are two electron processes. Depending on the substrate, the nucleophile and the reaction conditions, the mechanism of nucleophilic substitution varies.[14]

With some compounds, substitution reactions are very slow due to strain, steric and electronic factors. In such cases, nucleophilic substitution can be accomplished by mechanisms that involve ET steps.[15] For a compound to undergo ET mediated nucleophilic substitution reactions, a free radical or radical ion intermediate has to be formed by an initial ET process, which can be effected by different means. The most widely used methods include electrochemical initiation, thermal ET from an appropriate donor, usually a charged nucleophile and photoinitiated ET from the nucleophile. The latter two types of initiations are favoured between nucleophiles that are very good electron donors and substrates that are very good acceptors.

In the aromatic family, with substrates bearing an electron-withdrawing group (EWG), SNAr is usually the accepted nucleophilic substitution mechanism. Unactivated haloaromatics also react by this procedure when activated by complexation with chromium tricarbonyl. They can also react with strong bases to give substitution by the benzyne mechanism. Nucleophilic substitution can also be achieved from aromatic diazonium salts. Even hydrogen atoms can be substituted, under appropriate conditions, by a vicarious nucleophilic substitution. For this reaction to proceed, presence of

an EWG is also required. Halogen metal exchange is another well-established route to account for nucleophilic substitution of halobenzenes and alkyl halides, generally with nucleophiles derived from tin, silicon, and germanium.

Besides this relatively wide polar mechanistic spectrum, many systems have been shown to react slowly or to be unreactive through any of them. Their lack of reactivity is usually due to strain (cycloalkyl and polycycloalkyl halides), steric (cycloalkyl, polycycloalkyl, and neopentyl halides), electronic factors [unactivated aromatic and heteroaromatic substrates, vinyl halides, and perfuoroalkyl halides (R_fX)], or a combination of them. For these compounds nucleophilic substitution can be accomplished by mechanisms that involve electron transfer steps. In addition, there are families of compounds for which, although the polar and ET routes are feasible, the latter pathway is favoured. An example is alkyl halides substituted by π acceptor EWGs. For a compound to be substituted by ET, its radical has to be formed by an initial ET, which can be performed by different means. The most widely used are electrochemical initiation, thermal ET from an appropriate donor, usually a charged nucleophile, and photoinitiated ET from the nucleophile. The latter two types of initiation are favoured between nucleophiles that are very good electron donors and substrates that are very good electron acceptors. Once the radicals are formed, they can react through the SRN1 chain mechanism with radical and radical anions as intermediates (Scheme 1).



Scheme 1

Substitution by a nonchain SRN1 process has also been proposed, albeit in a considerably more limited number of cases. ET followed by the collapse of radicals within a solvent cage has been proposed as a possible mechanism for some thermally initiated substitution of alkyl halides. Between these two possible pathways the SRN1 is the one that has been most thoroughly tested with respect to its mechanistic characteristics and the one that has been shown to operate in most systems. This mechanism, known by the initials for Unimolecular Radical Nucleophilic Substitution, was first proposed independently by Kornblum[16] and Russell[17] in 1966 for the substitution of alkyl derivatives bearing EWG and a suitable leaving moiety. In 1970 Bunnett and coworkers[18] applied it to rationalize the substitution of unactivated aromatic halides (ArX).

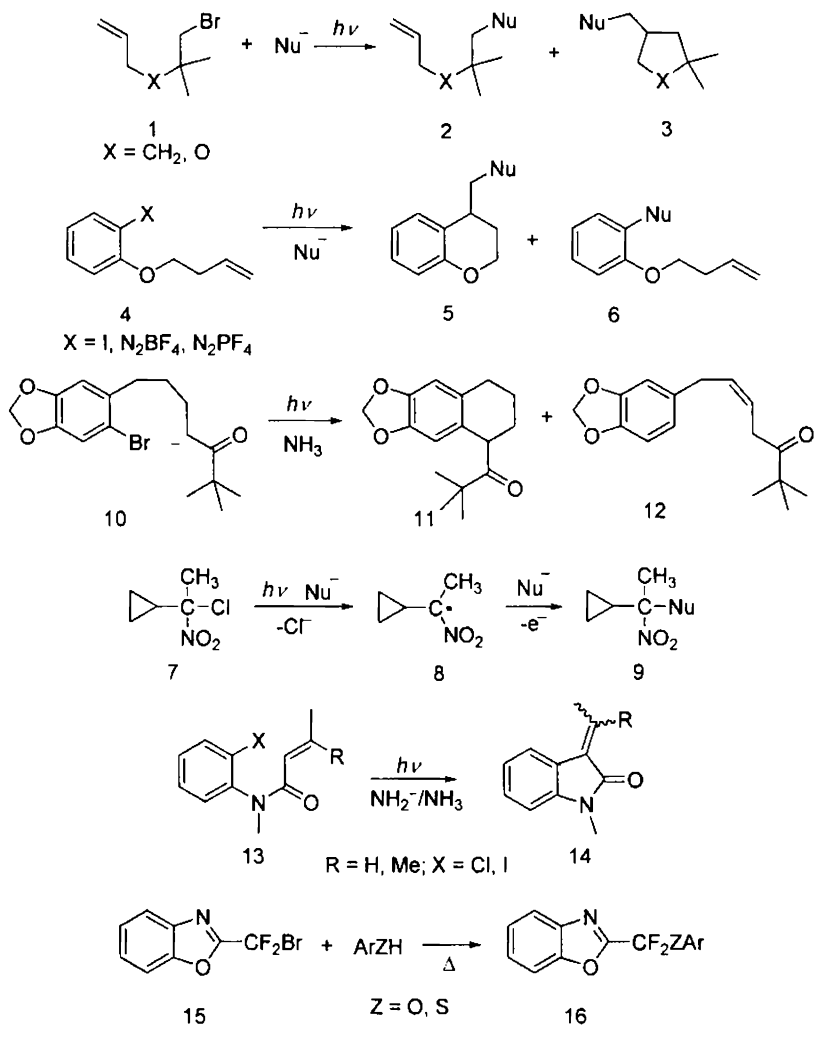
The process has a considerably wide scope in relation to substrates, nucleophiles (Nu^-), and synthetic capabilities. The most important substrates that participate are alkyl halides with EWG (nitroalkyl, nitroallyl, nitro- or cyanobenzyl, and their heterocyclic analogues, as well as quinone derivatives), unactivated aromatic and heteroaromatic substrates, vinyl halides, R_fX, cycloalkyl, polycycloalkyl, and neopentyl halides. In addition to halides, other leaving groups are known [i.e., $(EtO)_2P(O)O$, RS (R = Ar, alkyl), ArSO, $ArSO_2$, PhSe, Ph_2S^+, RSN_2 (R = *t*-Bu, Ph), N_2BF_4, R_3N^+, N_2^+, N_3, NO_2, and XHg]. Many substituents such as alkyl groups, OR, OAr, SAr, CF_3, CO_2R, NR_2, NHCOR, NHBoc, SO_2R, CN, COAr, and F are compatible with the reaction. Even though the reaction is not inhibited by the presence of negatively charged substituents such as carboxylate ions, other charged groups such as oxyanions hinder the process. In general, substituents such as NO_2 groups are not suitable for SRN1 substitution on aromatic substrates but are important EWG on aliphatic substrates, favouring the ET process.

Carbanions from hydrocarbons, nitriles, nitroalkanes, ketones, esters, *N,N*-dialkylacetamides and thioamides, and mono- and dianions from *β*-dicarbonyl compounds are some of the most common nucleophiles(Nu^-) through which a new C-C bond can be formed. The C-C bond formation is also achieved by reaction of aromatic alkoxides with aromatic substrates. On the other hand, *O*-alkylation is obtained by reaction of these anions and MeO^- ions with R-substituted nitroalkanes and *p*-nitrocumyl derivatives. Among the nitrogen nucleophiles known to react are NH_2^- ions, anions from aromatic amines, pyrrole, diazoles, and triazoles. These anions and the aromatic alkoxides show similar behaviours. Although they react with aromatic substrates to usually afford *C*-arylation, *N*-alkylation is the main reaction with alkyl halides bearing EWG. Anions from tin, phosphorus, arsenic, antimony, sulphur, selenium, and tellurium react through the heteroatom to form a new C-heteroatom bond. Carbonylation to afford the acid or ester derivatives is possible by reaction with cobalt carbonyl species. In this system substitution of ArCl and vinyl and alkyl halides is achieved in excellent yields.

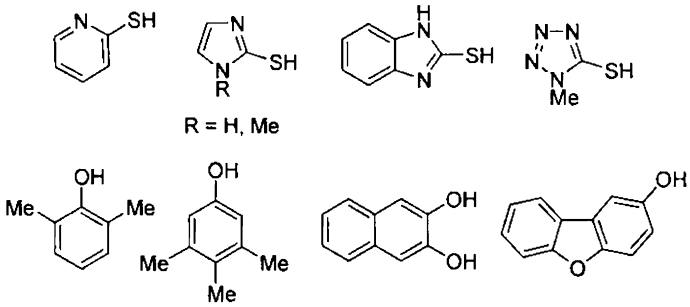
When the substrate has two leaving groups, disubstitution by the same Nu^- is possible. There are a few examples of tri- and tetrasubstitutions. Substitution by different Nu^- can also be achieved by a sequence of separate SRN1 reactions on appropriate ArX. Aromatic compounds substituted by three different Nu^- have been synthesized following this approach. More recently, the combination of the synthesis of stannanes by the SRN1 mechanism followed by a cross-coupling reaction with electrophiles catalysed by Pd(0) has shown to be an alternative synthetic approach to polyaryl compounds. Tri- and tetrasubstituted olefins can be synthesized by reaction of nitronate anions with alkyl halides bearing EWG due to the possibility of nitrous acid elimination from the substitution product.

The SRN1 mechanism has proved to be an important route to ring closure reactions, mainly in aromatic systems. The synthesis of indoles, isocarbostyrils, binaphthyls, etc, and an important number of natural products have been achieved by this process. Cyclization has also been reported in the reaction of alkyl halides with EWG. Several reviews have been published on the subject in relation to the mechanism of bond formation and bond breaking by ET,[19] substitution at activated[20,21] and nonactivated[20b,22] sp^3 carbons, SRN1 reactions at sp^2 carbons,[20b,23] aromatic photoinitiated substitutions,[20b,24] reactions performed under electrochemical catalysis,[25] and synthetic applications of the process.[26] Some examples are given in Scheme 2.

Thermal ET[27] is a possible initiation process, which depends on the relationship between the electron affinity of the substrate and the oxidation potential of the nucleophile. In light-induced ET reactions, photoexcitation of nucleophiles or substrates takes place. Electron transfer from either an excited state nucleophile to the substrate in the ground state or from the nucleophile in the ground state to substrate in the excited state is possible. Both these possibilities arise out of the dichotomous donor-acceptor properties of the excited states. Based on molecular orbital diagrams, it is easy to illustrate that a molecule in the excited state is a better electron donor as well as acceptor *vis-à-vis* the corresponding molecule in the ground state. For electron transfer processes in the excited state, changing the solvent and irradiation source affect the reactivity of substrate-nucleophile pair.



other nucleophiles :



Scheme 2

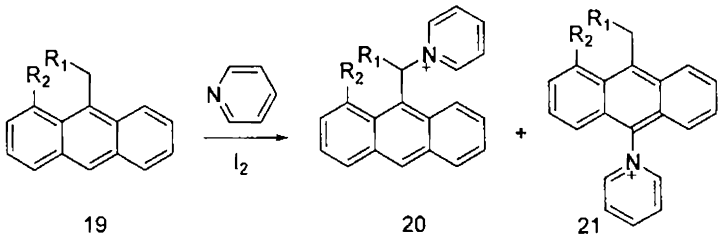
Addition of organometallics to a carbonyl compound is also an example for ET reaction[28]. In this case an electron is transferred from an organometallic reagent to the carbonyl compound. Though single electron transfer mediated steps are postulated for certain substrates that exhibit overall SN1/SN2 reactivity, only few reports exist on true electron transfer mediated nucleophilic substitution reactions in the aliphatic family. Nevertheless, in reactions involving highly electron deficient substrates and highly electron rich nucleophiles, single electron transfer mediated processes are highly probable.

Arylalkyl radical cations can partition along two mechanistically related channels. One involves proton loss, leading to side-chain oxidation, and the other involves nucleophilic attack, leading to ring oxidation. The rate of proton loss, the kinetic acidity, is apparently the key branch point between these two pathways and has been implicated in biooxidation pathways leading to carcinogenesis,[29] although not, apparently, in P450-mediated oxidations.[30] Arylmethyl radical cations are recognized to be very strong acids thermodynamically by those familiar with the work of Weller,[31] Arnold,[32] and Bordwell.[33]

Arnold's contribution was to recognize that the pK_a values for toluene radical cation (-12)[32] and 9,10-dimethylanthracene (-6)[33b,34] can be calculated by using thermodynamic cycle of the electron transfer process. Thus a strong thermodynamic driving force exists for rapid proton loss once the radical cation is formed, leading ultimately to the product of solvolysis. In this regard, alkylanthracenes and higher condensed aromatics represent groups distinct from the monoalkylbenzenes, for which hydrogen atom transfer dominates,[30a,35] and from alkylamines, whose acidities are too low for facile deprotonation.[36] Given the high thermodynamic acidity of radical cations,

one might question why this is not the exclusive pathway for one-electron oxidations. The answer is that deprotonation may involve significant entropic and enthalpic barriers. In some cases, for instance, proton transfer may even occur from the weaker thermodynamic acid.[37] Thus proton transfer reactions may be inhibited by a number of factors.

The dramatic difference in reactivity among 9-methylanthacene (9MA), acenanthrene (AA), and 9-ethylanthracene (9EA) suggests that stereoelectronic effect must be more compelling as shown by Tolbert and coworkers.[38] They further illustrated the effect by the nucleophilic attack on the radical cation formed in the above series. The exclusive formation of the product obtained through the nucleophilic attack on 10-C for 9EA shows the stereoelectronic control over the reaction (Scheme 3).



19	20	21
19a; $R_1 = R_2 = H$	a) 10%	a) 90%
b; R_1 = Me, $R_2 = H$	b) 0%	b) 100%
c; $R_1 = R_2 = -CH_2^-$	c) 76%	c) 24%
d; R_1 = MeSi, $R_2 = H$	d) 84%	d) 16%

Scheme 3

Several factors contributing to this strong stereoelectronic effect can be put forward. In the absence of stereoelectronic effects, alkyl substituents in AA and 9EA would stabilize the radical following deprotonation and thus enhance radical cation acidity. Such effects are evident in Russell's[39] elegant study of steric effects in phenyl radical abstraction of hydrogen in toluene, ethylbenzene, and indane where hydrogen atom abstraction from ethylbenzene is faster than that for toluene by a factor of 3. Tanko[40] has accounted that

relative rates of hydrogen abstraction by bromine atom for the series 9-methylanthracene, acenanthrene, and 9-ethylanthracene is exclusively dependent on stereoelectronic effect in the transition state.

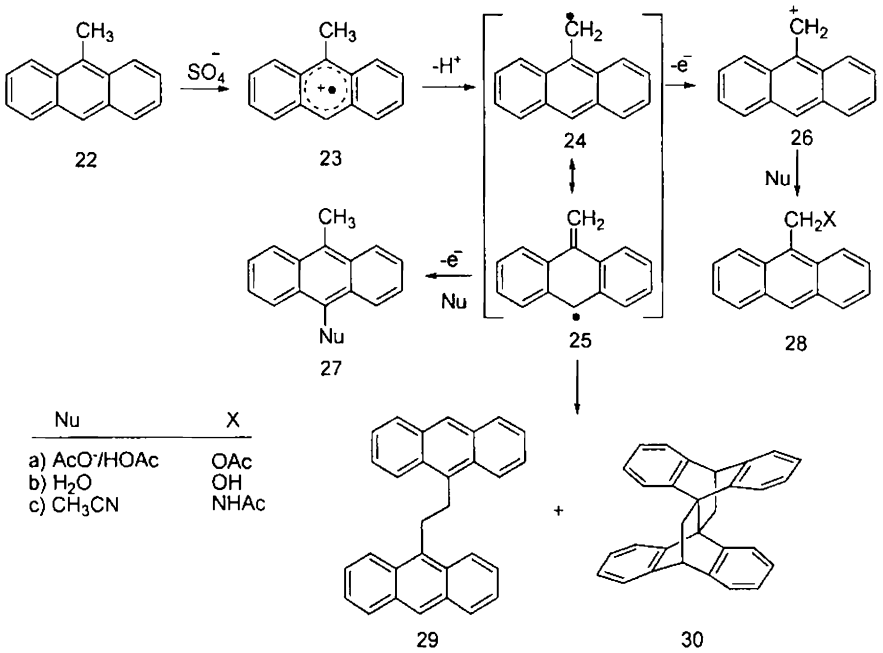
In nonaqueous solvents such reactions are known to be slow despite favourable thermodynamics, especially when carbon acids are involved.[41] For instance, proton loss from toluene radical cation is estimated to be 4 orders of magnitude slower in acetonitrile than in water.[42] For the radical cation of dimethylbenzylamine, proton loss occurs faster from the methyl group despite thermodynamically favoured loss from the benzyl group, an effect attributed to unfavourable steric interactions in the latter.[43] For hydrocarbon ions and radicals where stabilization is strictly governed by *p*-orbital overlap, the inability of the newly forming carbon free valence to achieve overlap with the *p*-orbital framework of the aromatic ring may prevent facile proton loss.

The idea of a stereoelectronic effect was given support by the observation that deprotonation of *p*-cymene (*p*-isopropyltoluene) radical cation occurs from the methyl group, not the isopropyl group.[44] This effect was attributed to the bisected conformation expected of the isopropyl group, preventing it from achieving the requisite planarity. More recently, Baciocchi[44] has pointed out that this hydrocarbon adopts a planar conformation in its radical cation state and has ascribed this result to steric hindrance to approach by base rather than to a stereoelectronic effect. It has been shown that stereochemistry of these reactions is solvent dependent, with increasing water concentration favouring deprotonation of the sterically more encumbered isopropyl group.[45]

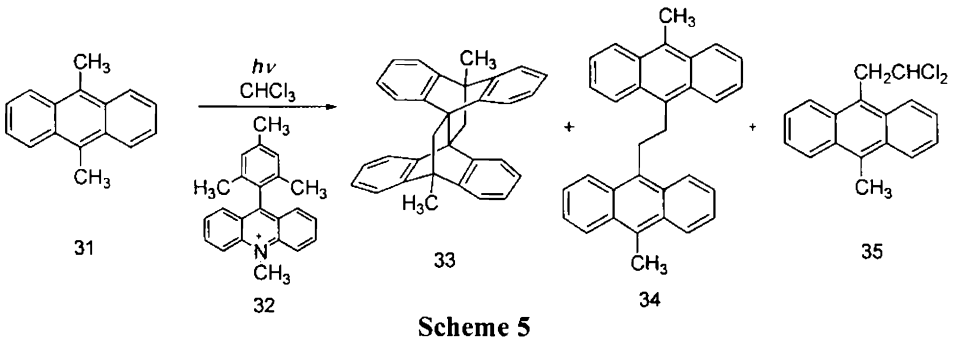
Nucleophilic attack on the radical cationic center formed through single electron transfer oxidations has been widely studied. Radical cations from several arenes and alkylarenes have been generated via single electron

oxidation using one electron oxidants such as Cu(II) and Ag(II) complexes of peroxydisulphate[46-52]. The radical cation formation and subsequent reactions of 9-methylanthracene is reported by Deardruff and coworkers.[53] The oxidations in acetic acid, acetonitrile under dry and aqueous conditions have resulted in nucleophilic substitutions giving rise to acetoxy derivatives (Scheme 4).

Another interesting report of photoinduced one electron oxidation of 9,10-dimethylanthracene (**31**) in chloroform using 9-mesityl-10-methylacridinium ion (**32**) shows the generation of radical cation which undergoes subsequent reactions such as dimerisation to give dimethyllepidopterene (**33**) and nucleophilic substitution reactions[54] (Scheme 5).

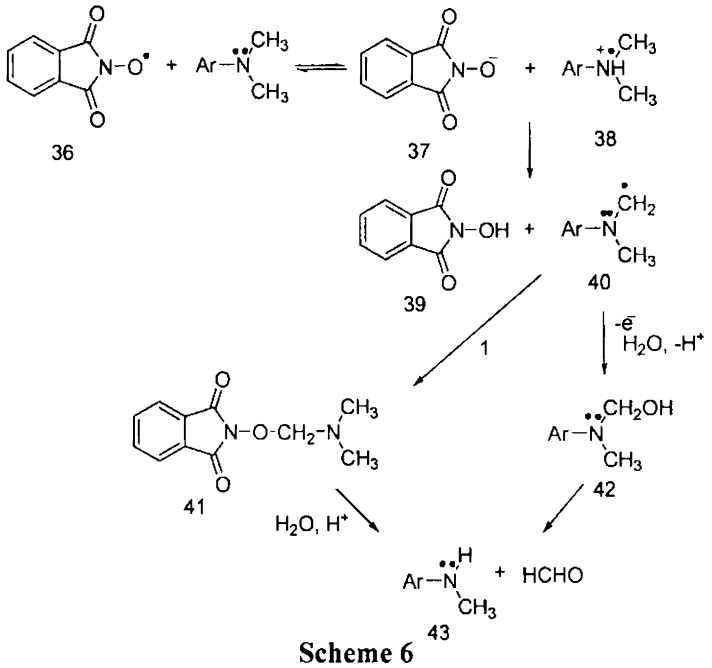


Scheme 4



Scheme 5

Electron deficient systems like phthalimide *N*-oxide radical[55] (**36**) and *N*-methylmaleimide[56] are well known to generate radical cations of various amines. In most of the cases studied, deprotonation at the β-carbon followed by either a nucleophilic attack or *N*-dealkylation is the major reaction pathway (Scheme 6). One electron oxidations of amines with $Cu(ClO)_4$ also have been widely studied in their perspective of radical cation generation and subsequent nucleophilic reactions.[57,58]



Scheme 6

1.4. Electron Transfer Reactions of Amines

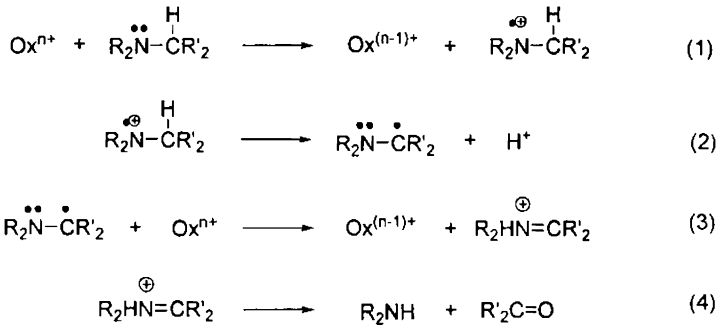
Amines and their derivatives are more widely distributed in nature than any other functional group family. This combined with the ease of oxidation of amines because of the lone pair of electrons on the nitrogen atom makes electron-transfer reaction of amines important in several electrochemical, photochemical and biochemical redox processes.[59-76] One electron oxidation of amines leads to the formation of radical intermediates that can be used for the synthesis of amino acids, alkaloids, and several other nitrogen-containing compounds of biological and pharmaceutical importance.[77-81]

Electron-transfer reactions of amines are also important in several technological applications such as imaging, photopolymerisation and fading of textile dyes.[82-86] More recently the electron donating capacity of amine functionality has been extensively used for designing new materials such as fluoroionophores, organic conductors, electroluminiscent materials, photovoltaics, and materials with nonlinear optical activity.[87-97] The mechanism of electron transfer reactions of amines has been studied by different methods, including the thermochemical, electrochemical, photochemical, and radiation chemical techniques.

Electron transfer reactions of amines can be initiated by a variety of chemical oxidants. One electron oxidation has been observed in reactions of amines, say, with metal salts such as ceric ammonium nitrate (CAN), manganese oxalate, alkaline ferricyanide, phenanthroline complexes of iron, oxacyanomolybdate.[81,98-104] The mechanism of electron-transfer catalysed reactions of amines by chlorine dioxide and permanganate have been intensively investigated in aqueous solutions.[103,105,106] In nonaqueous solvents, *N*-bromosuccinimide in carbontetrachloride and *N*-chlorobenzotirazole in benzene were reported to react with amines via single-

electron transfer (SET).[107,108] Metal ion catalysed oxidation of vinyl amines by molecular oxygen and of aromatic amines by nitrogen dioxide have been reported.[109-111] In the presence of transition metal ions, hydrogen peroxide and peracids are known to liberate hydroxyl radicals which react with amines either via electron transfer or hydrogen atom transfer.[112-116] It has been proposed that oxidation of amines catalysed by enzymes such as amine oxidases and cytochrome P-450 occur via SET process.[74-76] Reagents such as hydrogen peroxide, peroxy acid and ozone bring about two-electron oxidation of amines, usually resulting in the formation of amine oxides or hydroxylamines.[80]

Many studies of mechanism of oxidation of amines have been performed with chlorine dioxide or ferricyanide as oxidants as they have absorption bands with maxima at 357 and 420 nm, respectively. Changes in the absorbance at these wavelengths for the respective oxidants were used conveniently to follow the kinetics of the reactions. On the basis of these studies the electron transfer mechanism is proposed as in Scheme 7.[80]

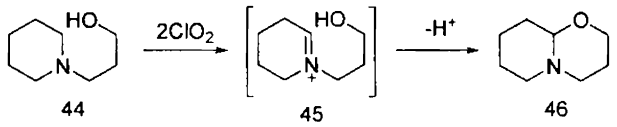


Scheme 7

The amine radical cation formed in the initial one electron transfer process deprotonates at the α-carbon and the amino alkyl radical formed is oxidized to the iminium salt which hydrolyses to the dealkylated amine and a

carbonyl compound. With the use of benzoyl peroxide as oxidant the aminium radical is also believed to be formed. In many of these reactions hydrogen-atom abstraction to yield the aminoalkyl radical directly is also feasible. Chlorine dioxide reacts with dibenzylamine by 35% hydrogen abstraction and 65% electron transfer.[117] Permanganate on the other hand reacts with triethylamine exclusively by electron transfer[106] whereas it reacts with benzylamines predominantly via hydrogen atom abstraction.[118] In the oxidation of benzylamines, apart from formation of the dealkylated amine and benzaldehyde, formation of imines, benzonitrile, diazines, anilines, and *N*-benzylidine benzylamines has also been observed.[119-125]

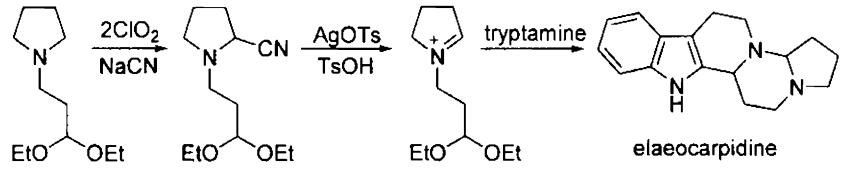
The α-aminoalkyl radicals as well as iminium ions generated as intermediates in electron-transfer reactions of amines can be used for bringing about synthetically useful transformations of amines. The synthetic applications of amine oxidation reactions are brought about by thermal, electrochemical and photochemical methods. Because of the relative instability of amine radicals, their synthetic applications in thermal one-electron catalysed reactions are rare. Aminium radicals generated *via* metal catalysed degeneration of chloramines and hydroxylamines can undergo a variety of synthetically useful reactions such as inter- and intramolecular addition of olefins and in aromatic amination reactions.[81,113] Chlorine dioxide catalysed cyclisaton of tertiary aminoalcohols to oxazilidines and tetrahydro-1,3-oxazines in basic aqueous medium has been reported[126] (Scheme 8).



44 45 46

Scheme 8

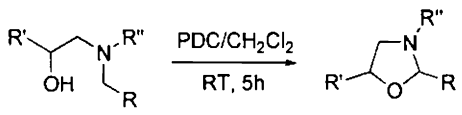
α-Cyanoamines are powerful synthons for the preparation of a variety of substituted piperidines. Reactions of ClO_2 with tertiary amines in presence of excess of aqueous sodium cyanide afforded α-cyano substituted tertiary amines in excellent yields. This strategy has been utilised for the synthesis of the alkaloid (±)-elacocarpidine (**50**) in moderate yields[126] (Scheme 9).



47 48 49 50

Scheme 9

Oxidation of *N*-aryl-*N*-methyl-substituted β-aminoalcohols using pyridinium dichromate (PDC) has recently been reported to give moderate to excellent yields of oxazolidines[127] (Scheme 10).



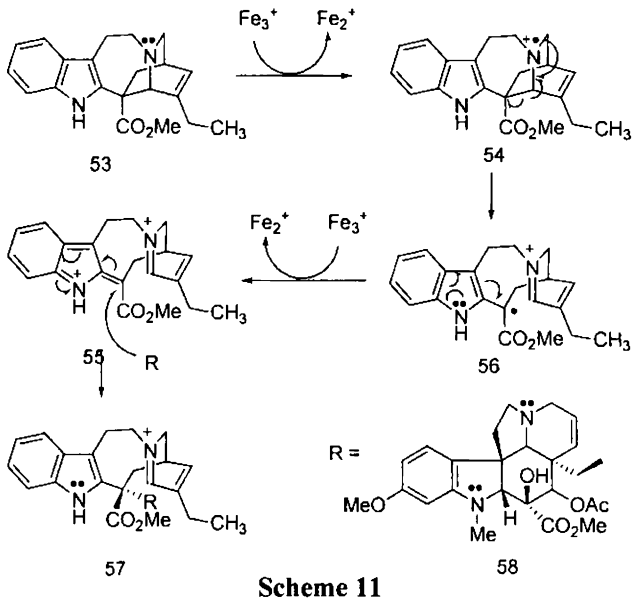
51 52

R = H
R' = Ph-CH2 ; alkyl
R''' = aryl

Scheme 10

Singlet oxygen has been reported to react with amines *via* an electron transfer mechanism.[128] Electron transfer catalysed reactions of alkaloids in the presence of cyanide ions, by singlet oxygen generated from 1,4-naphthalene endoperoxide lead to the formation of the corresponding α-cyano aminated products in good yields.[129] Ferric ion-induced coupling of catharanthine and vindoline in aqueous acidic media to produce 3,4'-anhydrovinblastine has been proposed to occur *via* the formation of a cation radical of the tertiary amine of catharanthine. Rearrangement and subsequent fragmentation

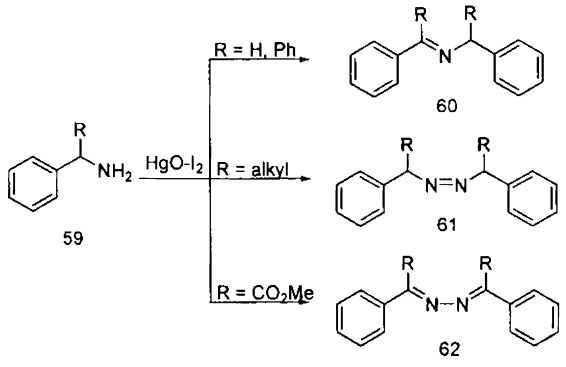
between C16 and C21 lead to ring opening. A second oxidation followed by nucleophilic attack of the diiminium ion by vandoline results in the formation of iminium ion which on borohydride reduction yields 3,4'-anhydrovinblastine[130] (**57**) (Scheme 11).



53 54 55 56 57 58

Scheme 11

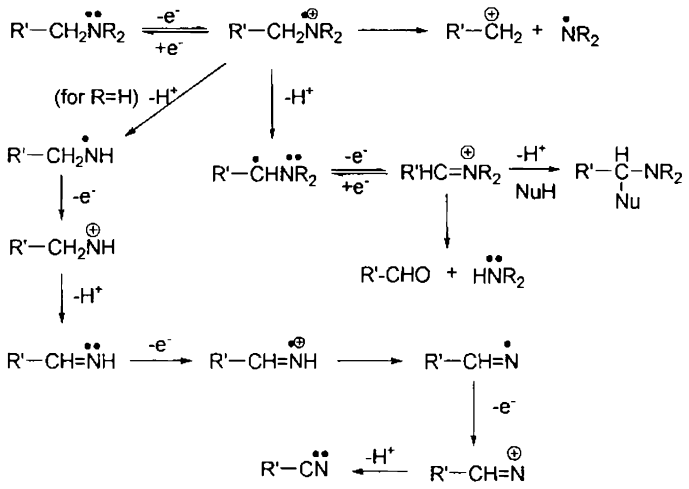
Metal oxide catalysed reactions of anilines and benzylamines have been utilised to synthesise azobenzenes and *N*-benzylidenebenzylamines in good yields[131-133] (Scheme 12).



59 60 61 62

Scheme 12

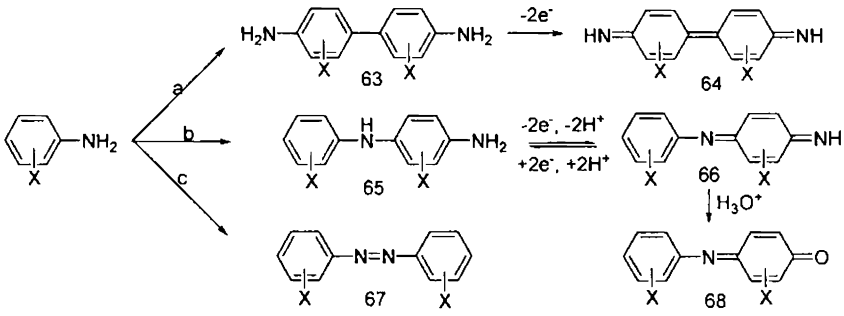
Electrochemical techniques are a convenient means of studying one-electron oxidations of amines. Electrolytic oxidation of amines result in the formation of an amine radical cation by one electron transfer to the electrode. The radical cation thus formed can under go C-N bond cleavage yielding a relatively stable carbocation that undergoes solvolysis, add to a nucleophile or polymerise. As observed in the thermal oxidation reaction, deprotonation at the α-carbon to yield the α-aminomethyl radical, followed by rapid oxidation to the iminium ion forms a major reaction pathway.



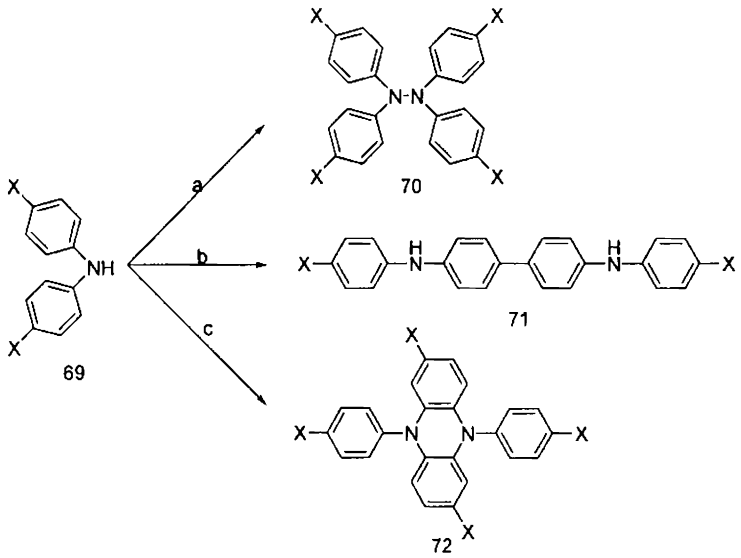
Scheme 13

For primary and secondary amines, nitrogen deprotonation can occur under strongly basic conditions. The resulting nitrogen centered radicals dimerise or undergo further oxidation to yield nitrenium ion (>N:$^+$). Use of silver or nickel electrodes leads to further oxidization to nitriles. Anodic oxidation of aromatic amines are rather complex and are substantially affected by the reaction conditions.[59-61,134-136] Scheme 13 shows the anodic oxidation of aniline and its derivatives.

Diphenylamines on electrooxidation also undergo aryl-aryl, *N*-aryl or N-N coupling as shown in Scheme 14 and 15. Short chain and reactive amines are easily oxidized by electrochemical methods at low temperatures whereas high temperatures are required for higher and less reactive amines.[59-61,137]

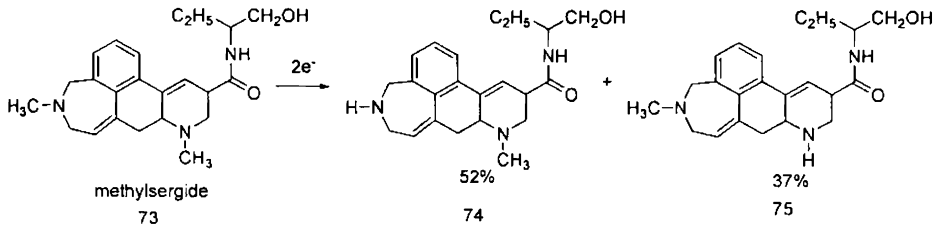


Scheme 14



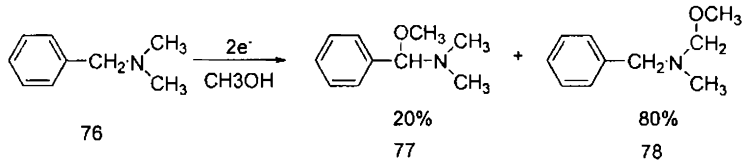
Scheme 15

The electrochemical dealkylation of aliphatic amines is a useful way of mimicking enzymatic dealkylaiton. This has been effectively used for the synthesis of *N*-dealkylated metabolites of drugs with much better efficiencies than the enzyme catalysed reactions[60] (Scheme 16).



Scheme 16

Nucleophilic substitution of the iminium ions formed in the electrochemical process provides a convenient route for the synthesis of α-substituted amino derivatives. The anodic oxidation of *N,N*-dimethylbenzylamine in methanol containing tetrabutylammonium fluoroborate or potassium hydroxide gives rise to methoxylated products (Scheme 17).

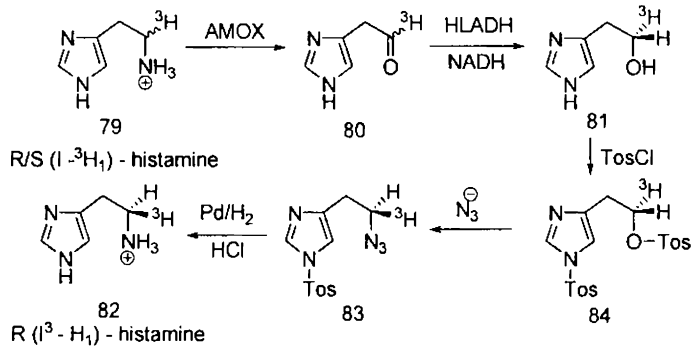


Scheme 17

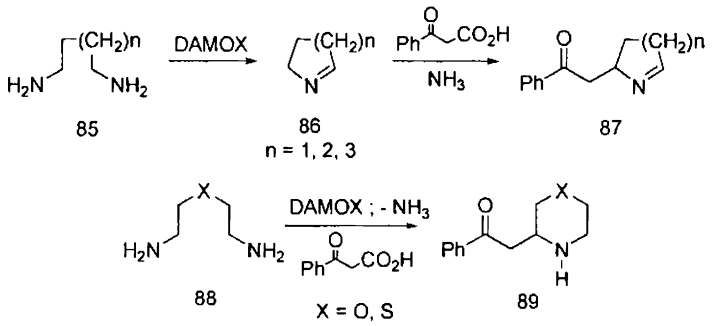
Electron transfer reactions of amines are of significant importance in biological systems. Enzymes known to catalyse the oxidative dealkylation of amines include monoaminase oxidase, cytochrome P-450, horseradish peroxidase, hemoproteins, and chloroperoxidase.[74-76, 138-142] *N*-dealkylation of amines by peroxidases are generally accepted to occur via one-electron transfer, whereas the role of electron transfer in reactions catalysed by enzymes such as monoamine oxidase and cytochrome P-450 is currently a topic of debate.

Enzyme catalysis also provides a convenient method for bringing about synthetically useful oxidizing transformations of amines.[143] The multistep synthesis of optically pure tritium labeled histamine involves an amine oxidase

reaction as the first step[144] (Scheme 18). Diamine oxidase (DAMOX) from pea seedlings catalyse the oxidative deamination of diamines. DAMOX-catalysed reaction of diamines in the synthesis of phenylacyl azaheterocycles is shown in Scheme 19.



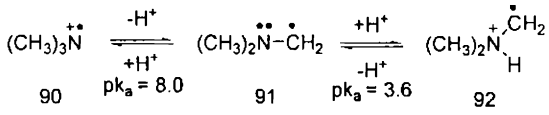
Scheme 18



Scheme 19

The resolution of racemic mixtures by amino acid oxidases also forms an important step in the synthesis of isotope labelled sugars and amino acids.[145] The mechanistic details of amine oxidation has also been extensively studied by use of radiation chemical methods.[146-151] The formation and subsequent reactions of amine radical cations by radiolysis which involves short-lived intermediates can be studied by pulse radiolysis in combination

with optical, conductivity, and ESR detection techniques.[146,147,149-151,152-153] Aminoalkyl radical intermediates formed in the process can be monitored optically because of strong absorbance in the 220-450 nm region. Apart form being good electron donors, the lability of the hydrogen atoms attached to the α-carbon of amines also make them very good hydrogen atom donors. However, the very high rate constant (k = 1.2 x 10^{10} $M^{-1}s^{-1}$) for the reaction of amines with hydroxyl radicals is strongly indicative of a predominantly electron-transfer mechanism[146] when compared to the rates with good hydrogen donors like formate (k = 3 x 10^9 $M^{-1}s^{-1}$) and isopropanol (k = 3 x 10^9 $M^{-1}s^{-1}$).[154] The radical cation formed in the electron transfer reaction is an oxidizing species whereas the α-aminoalkyl radical formed *via* hydrogen abstraction is reducing in nature. The amine radical cation of triethylamine formed in the radiolysis reactions can exist in an acid-base equilibrium (Scheme 20).

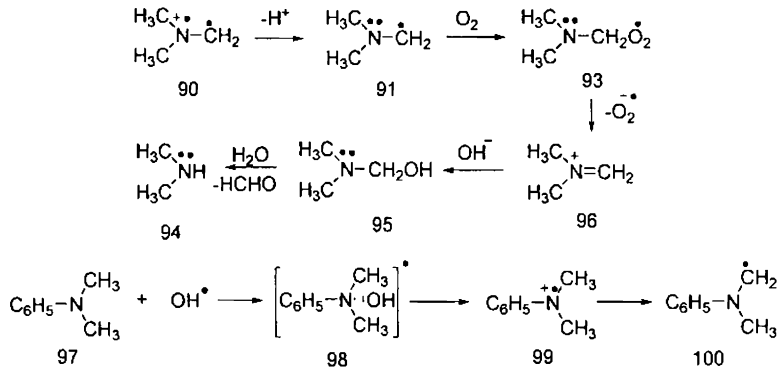


Scheme 20

The α-aminoalkyl radical reacts rapidly with oxygen (k = 3 x 10^9 $M^{-1}s^{-1}$) to form superoxide anion ($O_2^{\cdot -}$) and iminium ion possibly *via* a short lived (τ = 10^{-6} s) peroxy radical and further get hydrolysed to dealkylated/secondary amine in presence of a base. One electron oxidation of aniline by hydroxyl radicals yields the anilinium radical $[C_6H_5NH_2]^{+\cdot}$ which loses a proton over several microseconds to give the neutral radical $[C_6H_5NH]$ [155-156] (Scheme 21).

On the basis of studies using nanosecond time resolution, Holeman and Sehested suggested that the reaction of hydroxyl radicals with the

dimethylaniline occurs via the intermediate formation of a hydroxyl radical-amine adduct as described in Scheme 8.[157]



Scheme 21

1.5. Photoinduced Electron Transfer – PET

Photoinduced electron transfer is widely studied with regard to its potential applications in molecular electronics[158-161] and solar energy harvesting[162] as well as for developing a basic understanding of redox properties.[163-166] Though the ET reactions between donors and acceptors with both of them in the ground state are usually not favourable, photoexcitation of either of them often makes the ET processes to occur with reasonable rates.[167] Such photoinduced ET (PET) processes have the advantage that they can be initiated almost instantaneously by the use of ultra short laser pulses and thus the kinetics of the ET reactions can be investigated in real time. Measurements of this kind have made it possible to understand many details of the ET dynamics and thus to test the theoretical predictions with the experimental observations.[168-176]

The recognition of photoinduced ~~photoinduced~~ electron transfer (PET) as a key step in many photochemical reactions was fuelled by the Nobel Prize winning work of Marcus[177] and has, in recent decades, not only led to new

synthetic applications[178] but also to a general paradigm change in photochemistry. As has been described in detail in several reviews,[179] the energetics of light-induced electron transfer can be estimated by use of a simplified version of the Rehm-Weller equation.[180] Unlike many other physical equations, this relationship immediately displays its chemical relevance: electronically excited states are concurrently much better reductants and oxidants, and the actual redox behaviour depends on the reaction partner.

Electron-transfer quenching of potential excited-state acceptors including diverse molecules such as ketones, metal complexes, hydrocarbons, and dyes is a well-documented reaction.[181-189] Frequently used donors in these reactions include various tertiaryamines such as triethylamine.[189-194] Depending on the amine, the most often observed fate of photochemically produced radical cation in solution are back electron transfer or deprotonation; deprotonation at the α-carbon of tertiary amines produces a neutral but rather strongly reducing free radical which, after electron loss, gives an iminium ion which can often be hydrolysed to give a secondary amine and a carbonyl compound.[189,191,193-195]

The discovery and development of new photochemical processes has led to a considerable increase in the use of photochemistry for the synthesis of complex molecules. Increasing research activity in single electron transfer (SET) processes has focused not only on mechanism but also in discovering new synthetically useful reactions. Of particular interest is the use of iminium cations which are important electrophiles and are frequently used for preparing biologically active nitrogen heterocycles. In the absence of convenient procedures for generating regiospecific iminium cations for synthetic utilizations, a SET photocatalytic regioselective general procedure for *in situ* generation of iminium cation from 'acceptor'-amine pairs has been developed.

The remarkable advantages of this methodology are presented in connection with the synthesis of various biologically active alkaloids.

Carbonylamine systems play a major role in the key steps involved in the synthesis of various nitrogen containing heterocyclics and natural products.[196] The high-lying lone pair at N and the low-lying antibonding π_{CO}^* of the carbonylamine system render the amine-carbonyl combination suitable for frontier molecular orbital (FMO)-controlled nucleophile-electrophile ground-state interaction (Figure 1).

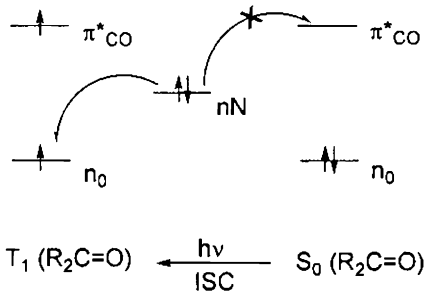
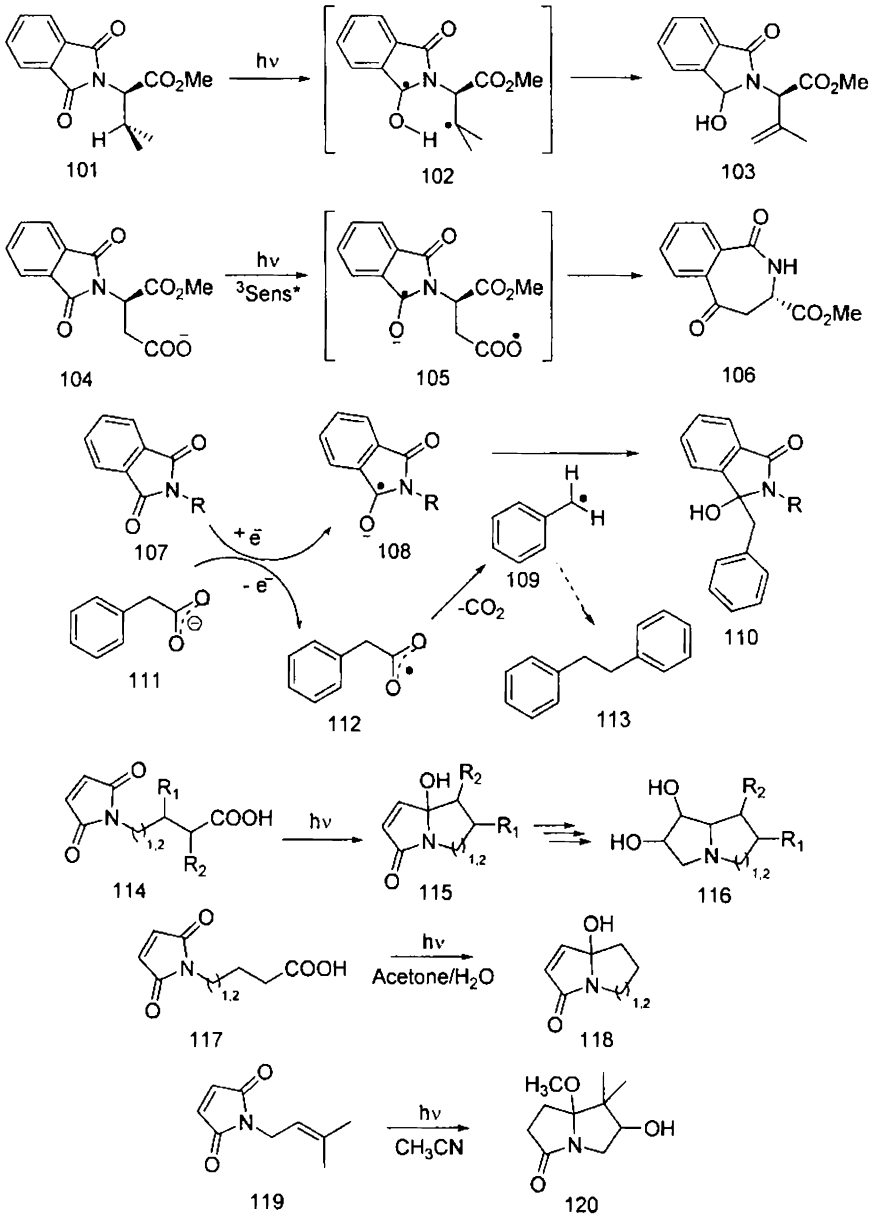
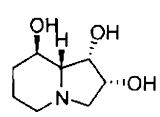


Figure 1

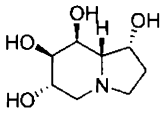
However, only after electronic excitation to the n→π* carbonyl state does an exergonic electron transfer become feasible. The same is true for less active electron donors like alkyl carboxylates (*vide infra*), unsaturated or strained hydrocarbons, aromatic compounds, and many more. Some synthetically useful examples are given in Scheme 22 and Chart 1.



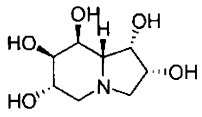
Scheme 22



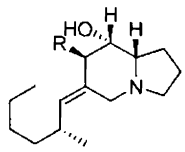
(+)-swainsonine



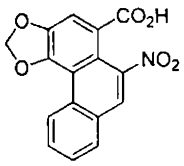
(+)-castanospermine



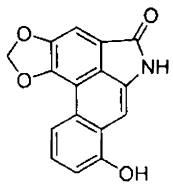
uniflorine A



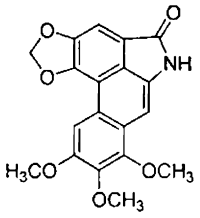
(+)-pumiliotoxin 251 D (R=H)
(+)-allopumiliotoxin 267 A (R=OH)



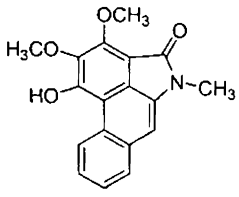
aristolochic acid II



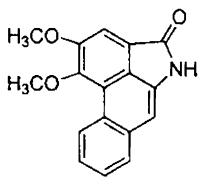
aristolactam Ia



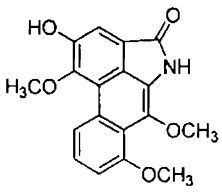
9-methoxyaristolactam IV



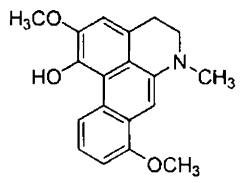
piperolactam E



cepharanone B



enterocarpam I



bulbocapnine

Naturally occurring indolizidines and phenanthrene lactams.

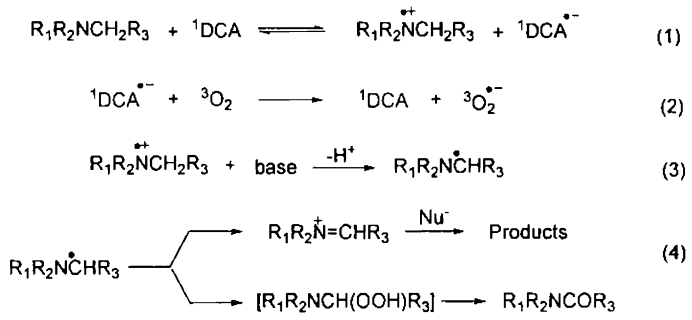
Chart 1

Photoinduced electron transfer (PET) reaction from electron acceptor sensitiser-amine complexes produces a radical anion and planar amine radical cation.[197,198] The overall thermodynamics of the reaction unambiguously and exclusively are in favour of electron transfer for many sensitiser-amine pairs. The rate constants are sensitive to electronic energies and reduction potentials of the sensitisers and oxidation potentials of the amines, as well as the structures of both sensitisers and amines.[199]

In general, amines with low ionisation potentials such as tertiary amines are the most effective electron donors. Among these factors, the reactivity of

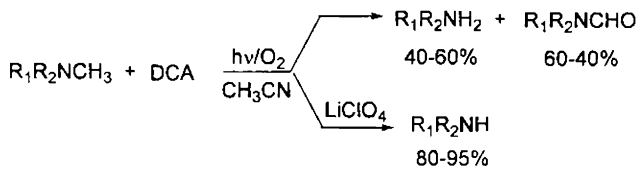
PET reaction is dependent on solvent polarity[200] and, the question is whether the primary intermediate is a solvent separated ion pair (SSIP) or a contact ion pair (CIP). The SSIP is more stable in polar solvents[201] and in these solvents the highly solvated ion radicals separate to form free radical ion pairs (FRIP).[202] The most general pathways available to these reactive amine radical cation intermediates is probably the fragmentation to ions and neutral radicals. In particular, fragmentation of cation radicals leading to radical and cationic species is a well studied subject.[203]

A number of studies have demonstrated that amine radical cation undergoes efficient proton loss and carbon-carbon bond cleavage at sites adjacent to nitrogen[204]. Proton loss from simple tertiary amines to generate an α-amino alkyl radical is a common feature. Thus, it was envisaged that the SSIP formed between 9,10-dicyanoanthracene (DCA)-tertiary amine pair will dissociate into FRIP in the medium of high polarity such as acetonitrile. In the presence of molecular oxygen, the SET process is a photocatalytic general method for iminium cation generation (Scheme 23).

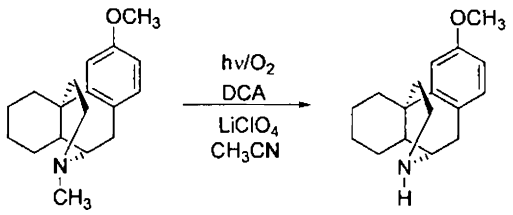


Scheme 23

In acetonitrile, all tertiary amines quench DCA fluorescence at the diffusion-controlled rate[205] and the amine radical cation is generated by electron transfer from amine to ^{1}DCA* (Schemes 24 and 25).



Scheme 24

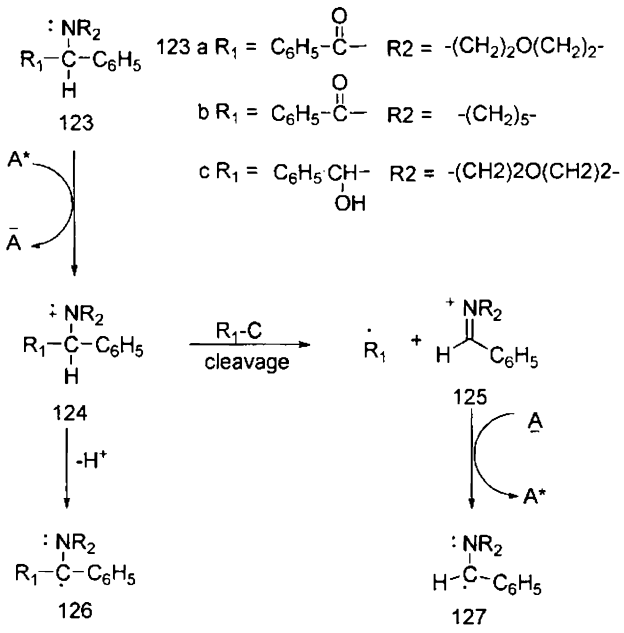


Scheme 25

The deprotonation of tertiary amine radical cations involves reaction of carbon acids, which might be anticipated to be relatively slow; however, laser flash spectroscopic investigations indicate this process can occur extremely fast, on the picosecond scale.[193]

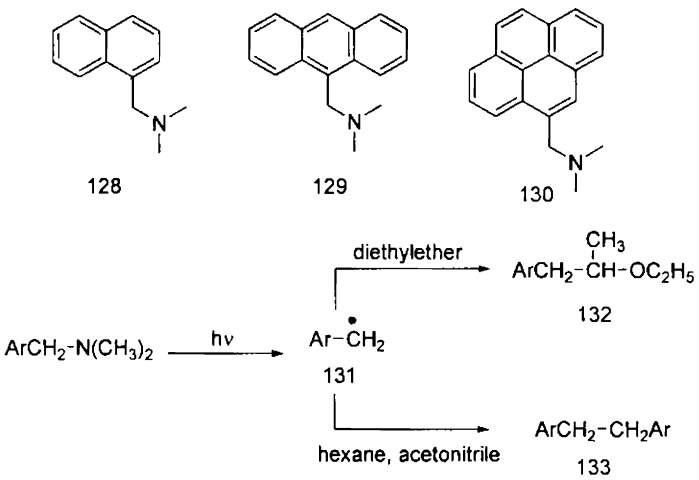
An alternative fate of reactive amine radical cations could be cleavage of a carbon-carbon σ bond α to the nitrogen; this reaction (Scheme 26) leads to a neutral free radical and a different iminium ion from that indicated above. Related C-C bond cleavage reactions have been observed for cations generated from ethers in solution,[206] for strained or otherwise reactive hydrocarbon radical cation,[207-210] or for certain amines in the gas phase (mass spectrometer).[211] Irradiation of **123a** or **123b** with ultraviolet light ($\lambda \leq 330$ nm) in the presence of polymerisable monomers such as methyl methacrylate resulted in rapid polymerisation; presumably the polymerisation was initiated by cleavage of the substrates by a Type I reaction to afford radicals (eq 1).[212-215]

$$C_6H_5COCH(NR_2)Ph \xrightarrow{h\nu} C_6H_5\dot{C}O + C_6H_5(NR_2)\dot{C}H \qquad (1)$$



Scheme 26

The photoinduced electron-transfer-mediated σ bond cleavage should be applicable for a variety of donors with appropriate substituents on the α-bond terminal carbons. Schneider and coworkers[216] found that irradiation of the (aminomethyl)arenes **128-130** in deoxygenated hexane or acetonitrile solution resulted in the formation of methyl arenes and 1,2-diarylethanes **133** as the major products. Irradiation in ether solvents resulted in the formation of solvent adducts. These products are presumed to be formed *via* photolysis of the arylmethylene-nitrogen bond to yield the arylmethyl-dimethylaminyl radical pair which can disproportionate to yield the methyl arene or undergo cage escape. The resulting arylmethyl radical can abstract hydrogen from the solvent, dimerise to yield the 1,2-diarylethane, or react with solvent-derived radicals (Scheme 27).

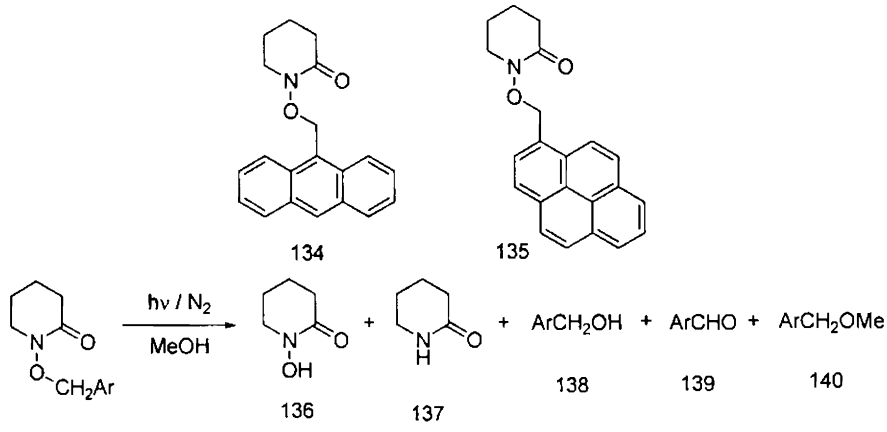


Scheme 27

Photochemical control of homolytic versus heterolytic bond-cleavage modes has been the subject of extensive research efforts because of its potential application to developing hybrid-type photoinitiators enabling the simultaneous progress of radical and cationic polymerisations.[217-225] Through comprehensive mechanistic studies on the photolysis of arylmethyl esters in nucleophilic solvents, Pincock and co-workers have shown that the dominant primary step is homolytic C–O bond cleavage from the singlet excited state to form a radical pair, electron transfer in which eventually gives an ion-derived product along with a radical-derived one.[220-224]

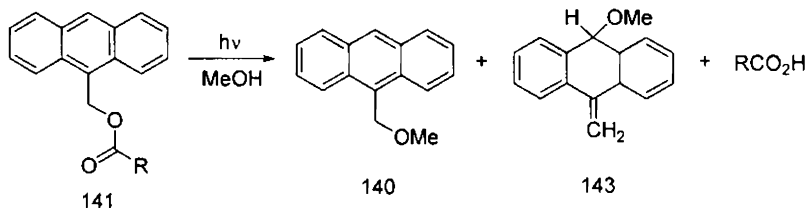
In the course of systematic study toward the characterisation of the excited-state behaviour of cyclic hydroxamic acid derivatives, it was found that bichromophoric 1-benzyloxy-2-pyridone in the singlet excited state undergoes homolytic N–O bond cleavage exclusively, giving benzaldehyde and 2-pyridone as major products along with a minor amount of benzyl alcohol.[225]

It was shown through analyses of the ground-state conformations for 1-benzyloxy-2-pyridone and related compounds, as well as of the deuterium isotope effects on the quantum yield, that the reaction proceeds mainly through a folded conformation but not a stretched one.[226] The replacement of the phenyl group in the bichromophoric molecule by the anthryl or the pyren-1-yl group was found to substantially enhance a charge transfer-type interaction between the two chromophores in the singlet excited state, affecting the bond-fission process of these *O*-substituted cyclic hydroxamic acids. In order to explore the possibility of photochemical control of heterolytic *vs.* homolytic bond scission in bichromophoric 1-hydroxy-2-pyridone derivatives having a 9-anthryl or a pyren-1-yl pendant, Yoshioka and coworkers[227] designed and synthesized 1-(9-anthrylmethyloxy)-2-pyridone (**134**), and 1-(pyren-1-ylmethyloxy)-2-pyridone (**135**) and demonstrated that these bichromophoric 1-(arylmethyloxy)-2-pyridones having a strong ability to form an exciplex intermediate undergo novel heterolytic cleavage of the C-O bond in competition with the homolysis of the N–O bond in their singlet excited states (Scheme 28).



Scheme 28

Tanaka and coworker[225] were successful in controlling two bond cleavage modes in the irradiation of various *O*-acyl anthracene-9-methanol and reported the formation of α as well as *p* substituted products (Scheme 29).



141 140 143

R = (4-Anisoyl)-, Acetyl-, Benzoyl-, (4-Toluoyl)-, (4-Cyanobenzoyl)-

Scheme 29

To rationally design a molecule-based device, it is critical to understand the role of the surrounding environment on electron transfer. Many previous studies have focused on the role of solvent on electron transfer processes.[228-239] In highly polar media, many cyclic photochemical electron transfer reactions obey the mechanism shown in Figure 2.[240] Singlet excited donors D are quenched by ground state acceptors A at or close to the diffusion-controlled rate and generate solvent-separated geminate singlet radical ion pairs. Due to magnetic interactions of the electron and nuclear spins the singlet pairs undergo partial intersystem crossing to their isoenergetic triplet states. In nanoseconds, diffusive reencounters lead to reverse electron transfer. Thereby, singlet pairs regenerate the ground state while from triplet pairs excited triplet donor molecules are obtained. Free ions are formed from pairs which escape the geminate processes. They undergo the reverse electron transfer upon diffusive encounters on a much longer time scale of micro-to-milliseconds. Such systems have been studied with various techniques including chemically induced dynamic nuclear polarization (CIDNP).[241-247]

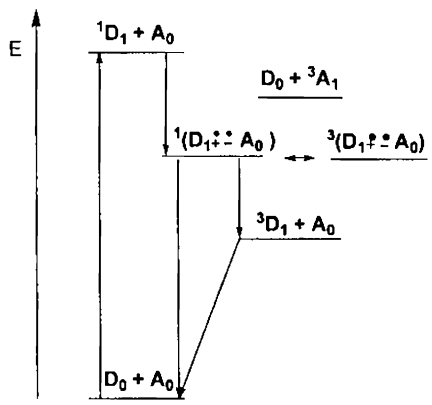


Figure 2

Figure 1. Energy level diagram for the photosystems *N*,*N*-dimethyl- 1-naphthyloamine/benzonitrile and 1,4-dimethoxynaphthalene/dicyanobenzene.

1.6. Electron Transfer Reactions of Sulphanes

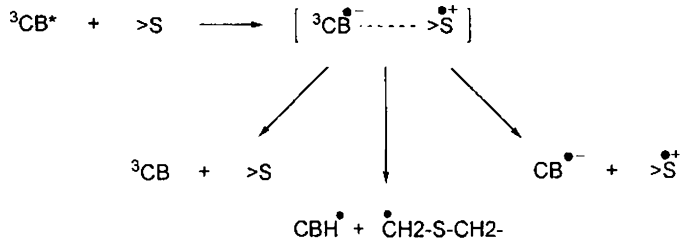
Free radicals and radical ions, having their unpaired electrons mainly on sulphur atoms, play unique roles in diverse areas of chemistry. They are important intermediates for specialized organic synthesis.[247-249] In oxidative stress,[250] they are implicated in the early stages of oxidative attack associated with aging[251] and with pathologies such as Alzheimer's disease.[252] Sulphur centered radicals are also involved in environmental issues.[253-255] Recently sulphur-centered radicals derived from co-initiators have proven to be effective in photopolymerisations.[256] Sulphur radical cations from thioethers are quite reactive, which raises the question of how oxidative damage can be stabilsed in oxidative stress.[252] On the other hand, it is the reactivity of the sulphur radical cations that is important in photopolymerisation.[256]

The photoreactions of sulphur-containing amino acids with 4-carboxybenzophenone have received some attention[257,258] because of the biological importance of these substrates and the model character of these reactions for the damage of cell components.[258a] While these molecules

contain two possible donor sites, the thioether group and the amino function, the observation of dimeric radical cations $[>S\therefore S<]^+$ has provided evidence in several cases that the electron is transferred from sulphur.[258a] Apart from decarboxylation of the sulphur-centered radical cations, deprotonation at α-carbon by the sensitiser anion to give an R-thioalkyl radical, which amounts to a net hydrogen abstraction, also plays some role.[258] The mechanisms of these photoreactions are therefore rather complex and involve several paramagnetic intermediates.

Charge-transfer processes involving organic sulphur compounds are of particular interest in biology and chemistry because transient sulphide radical ions can alter or protect the functional properties of enzymatic complexes or proteins.[259-262] During the past decade, the photochemistry of sulphur-containing molecules has received considerable attention. Research works are mainly devoted to the stabilisation of charged sulphides in dilute glass matrices, the creation of Rydberg series, and oxidation state-selected ionising of the gas phase by resonantly enhanced multiphoton ionization.[263-267] Photoexcited organic sulphides produce different responses which can lead to bond scissions or ionisation channels. The primary processes triggered by UV excitation of liquid organic sulphides correspond to S-S or C-S bond scissions and yield multiple radicals such as methyl thiyl radical or thioformaldehyde.[268-270] These bond breakings can compete with ultrafast electron photodetachment processes. Indeed, the ionisation process can induce a complex radical chemistry including either an electron solvation or an electron attachment on sulphur molecules with the formation of disulphide anion or cation radicals. These radicals characterised by three-electron two center bonds can be produced by ion-molecule reactions, [271,272] and play a significant role in chemistry.[273,274]

Filipiak and coworkers[275] have shown that sulphur radical cations can be used to generate carbon-centered free radicals that can initiate free radical polymerisation. The mechanism describing the primary photochemical processes involved in the electron-transfer quenching of the triplet state of 4-carboxylbenzophenone (CB) by sulphur-containing organic compounds has been studied.[276] The general reaction mechanism is shown in Scheme 30. After an initial formation of a radical ion pair, there are three main channels of its decay: (i) back electron transfer to form the reactants in their ground states, (ii) proton transfer within the radical ion pair to form the ketyl radical ($CBH^{\bullet}$) and an R-alkyl thioalkyl radical, and (iii) formation of free ion radicals to form $CB^{\bullet-}$ and the sulphur-centered radical cation ($S^{\bullet+}$, which will stand for S^{-}-centered radical zwitterions.



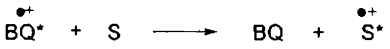
Scheme 30

Further secondary reactions depend on the structure of the sulphur-containing organic compounds used.[275] In the work done by Filipiak and coworkers, the organosulphur compounds included compounds like *S*-benzylthioglycolic acid and 4-(methylthio)phenylacetic acid where the formation of *S*-centered radical zwitterion was shown to take place.

Historically, organosulphur cation radicals have occupied a prominent place both in ESR and organic chemistry literature.[277] Several sulphur-containing compounds like thiaanthrene, phenothiazene, thioxanthen-9-one, dibenzothiophene, 4,4'-thiodiphenol, thianaphthalene undergo charge-transfer

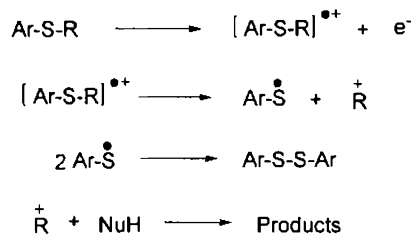
reactions with benzoquinone radical cations ($BQ^{\cdot+}$) generated in trifluoroacetic acid. The concept of charge transfer involving organometallics in organic reactions has long been recognised[278,279] and recently the potential of combined ESR and CIDEP (chemically induced dynamic electron polarization) techniques in providing unequivocal evidence of the nature of the charge-transfer processes in the photochemical reactions between quinones and organotins were convincinglydemonstrated.[280,281]

Depew and coworkers[282] showed that two organosulphur radical cations, thianthrene and phenothiazine, both form radical cations thermally in trifluoroacetic acid, but their concentrations are further enhanced upon addition of benzoquinone. On the other hand, thianaphthene radical cations are produced only when benzoquinone radical cations are present. Application of benzoquinone radical cations charge-transfer technique permitted observations of CIDEP from other less stable radical cations such as the thianaphthene.



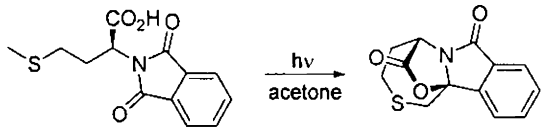
Scheme 31

One of the easiest ways to generate a carbenium centre is through an electron transfer activation of the sulphide group to give a reactive radical cation (Scheme 32). Such mild conditions have been elegantly developed by Amatore and Sinay[283] for the preparation of *O*-glycosides and disaccharides; both chemical and electrochemical activations were used.



Scheme 32

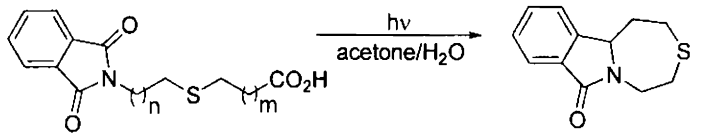
Kanaoka and coworkers[284] developed the concept of electron-transfer-initiated macrocyclisation for thioalkyl-substituted phthalimides. Later, Geriesbeck and coworkers investigated such processes when trying to develop a method for the synthesis of cyclic peptides from sulphur containing oligopeptides. In the photocyclisation of *N*-phthaloylmethionine (**144**) (Scheme 33), upon irradiation in pure acetone, tetracyclic lactone **145** was formed in high yields.[285] This reaction is unusual in the sense that photolysis of unprotected *N*-acyl amino acids normally leads to efficient decarboxylation. Thus, electron-transfer reactions involving thioalkyl groups can efficiently compete with carboxylate activation.



144 145 74%

Scheme 33

The yields of the photocyclisation products depended on the point of linkage and the spacer between the sulphur and the carboxylate group, indicating that for compounds with longer spacers between sulphur and the carboxylate anion, alternative photochemistry competes with or completely suppresses decarbonylation (Scheme 34).



146 147 74%

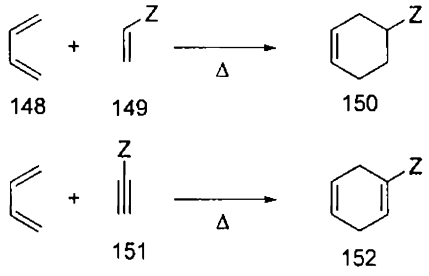
Scheme 34

	n =	m =	yield	ringsize
a	0	0	95	5
b	0	1	20	6
c	1	0	61	6
d	1	1	11	7
e	2	0	62	7
f	2	1	15	8
g	3	0	64	8

1.7. Diels-Alder Reaction

Bicyclic compounds[286] are of great importance since they constitute the basic structural framework of several compounds which are used as potential therapeutic agent against HIV and metastasis,[287] anticancer drugs,[288] anti-thrombotic compounds,[289] therapeutic agents for diseases[290] of the central nervous system etc. Diels-Alder reaction[291] is one of the major synthetic strategies employed to generate bicyclic compounds. Otto Paul Hermann Diels and Kurt Alder were awarded the Nobel Prize in Chemistry in 1950 for their work on this reaction. Diels-Alder reaction is generally considered the "Mona Lisa" of reactions in organic chemistry since it requires very little energy to create the very useful six-membered ring. [292-295] Since its formulation in 1928,[296] the utility of Diels-Alder reaction has remained inestimable for the synthesis of monocyclic as well as polycyclic compounds. It provides an unparalleled strategy for the regioselective and stereospecific introduction of multiple centers of configuration.

Diels-Alder reaction can be categorised as a cycloaddition between a conjugated diene and a substituted alkene or acetylene, commonly termed the dienophile to form a substituted cyclohexene system.[297-299] The reaction can proceed even if some of the atoms in the newly-formed ring are not carbon. Typically, the Diels-Alder reaction works best when either the diene is substituted with electron donating groups like -OR, $-NR_2$, etc or when the dienophile is substituted with electron-withdrawing groups like CHO, COR, COOH, COOR, COCl, COAr, CN, NO_2, Ar, CH_2Cl, CH_2NH_2, CH_2CN, CH_2COOH, halogen or C=C etc.[300]

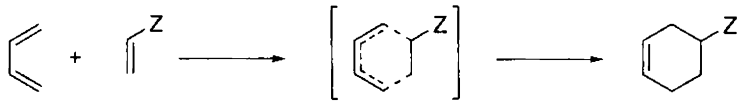


Scheme 35

Nearly all conjugated dienes will react with appropriate dienophiles. By varying the type of diene and dienophiles, many different types of ring structures can be synthesised.

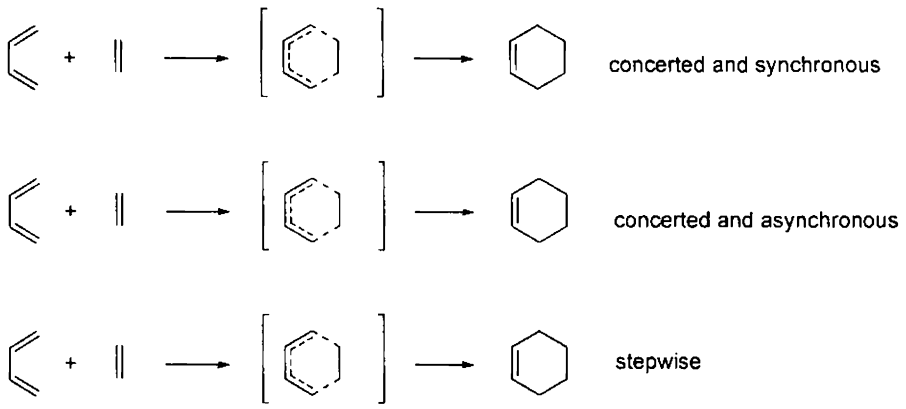
The mechanism of this reaction has been the subject of a long, complicated and even sometimes acrimonious debate. The six π-electrons of the two starting compounds form a common electron cloud in the field of six nuclei, similar to the aromatic sextet (a quasi-aromatic transition state). This aromatisation effect brings the transition state to a lower point on potential energy curve and consequently the reaction has comparatively low activation barrier. For nonsymmertic substituted dienes and dienophiles, several six-membered transition states can be envisioned and they differ substantially in

energy content. As a result, the Diels-Alder reaction typically leads to the exclusive, or at least preferential, formation of one of several possible isomers with respect to the positioning or orientation of the substituents. The reaction course is well accounted for in terms of the Woodward-Hoffmann concept of conservation of orbital symmetry. Its final outcome is generally predictable even for complicated cases.



148 149 150

Scheme 36

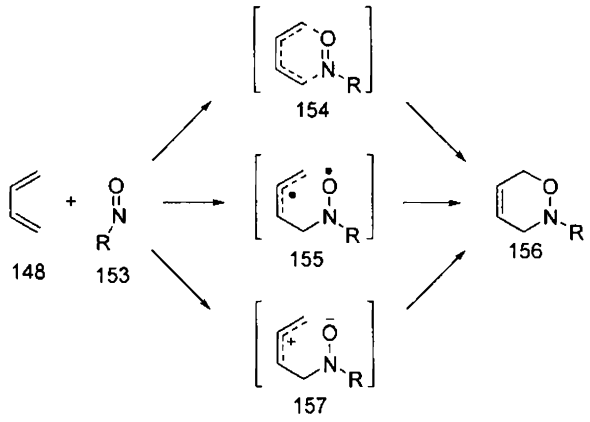


Scheme 37

The non-concerted and concerted asynchronous mechanisms show diradical intermediates, whereas the concerted synchronous mechanisms does not. One of these ideas is supported by a kinetic study done by Dewar and Pierini in 1984.[301] This experiment suggests that the reaction is concerted and synchronous. This conclusion was confirmed by doing a reverse Diels-Alder reaction involving maleic anhydride with furan, 2-methylfuran and 2,5-dimethylfuran. This experiment was based on the premise that since reactions

of unsymmetrical dienes or dienophiles have unsymmetrical transition states, there is no evidence to suggest that the same is not true for symmetrical dienes or dienophiles.

In 2001 Leach and Houk[302] did a study applying density functional theory to the transition states and mechanisms of Diels-Alder reactions involving a variety of nitroso compounds as dienophiles with butadiene and a variety of 1- and 2- substituted dienes. The reaction's activation and reaction energies as well as its stereoselectivities and regioselectivities were theoretically predicted and then compared to known experimental data. The general mechanism of the Diels-Alder reaction was found to be concerted and asynchronous. Here is a diagram from the original article of possible mechanisms involving the reaction between a nitroso compound with butadiene.



Scheme 38

This diagram shows that the pathway on the top is a concerted [4+2] cycloaddition with that particular transition state that is showed above. The pathway in the middle shows a possible diradical transition state. And the one down below shows a possible zwitterionic transition state. The study

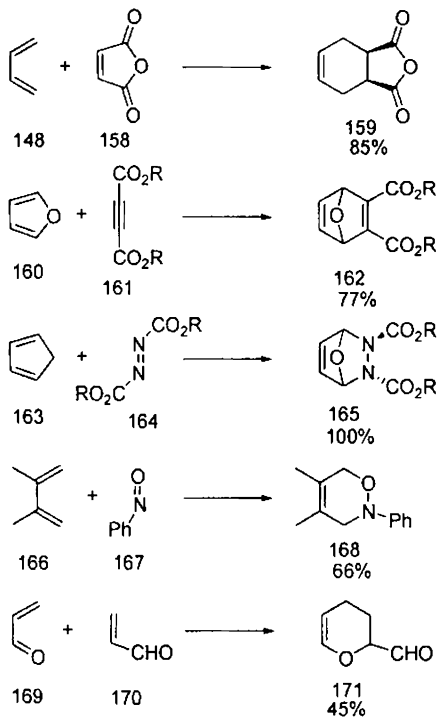
concluded that diradical and zwitterionic transition states only complete with each other when nitroso compounds with small amounts of nitrogen react with dienes that have substituents that stabilize radicals. According to this study, the asynchronicity of these concerted reactions may be due to the lack of symmetry of the nitroso dienophile. This study also concluded that Diels-Alder reactions involving nitroso compounds show a strong preference for *endo* products, which may be due to the lone pairs of the nitrogen and oxygen being electrostatically repulsed by the electron rich diene.

Using a simple level of quantum mechanical electronic structure calculation, several aspects of reactivity in this system can be explored. Nowadays, computational methods are able to access the transition state region directly, thus rendering partly obsolete the need to derive its properties from those of the frontier orbitals. The first step is to locate the transition state for the parent reaction. The final step will be to consider the effect of substituents, and in particular to derive one of the rules for regioselectivity, by considering the competing pathways in the addition of dienophile to the diene.

To assess properly the exclusive synthetic merits of the Diels-Alder reaction, it is necessary to consider the main peculiarities of its regio- and stereocourse. Diels-Alder reactions can lead to formation of a variety of structural isomers and stereoisomers (enantiomers and diastereomers).[303] Identity of major products can usually be predicted, however.

It must be emphasized that the very mechanism of this converted cycloaddition implies complete retention of configuration of the substituents of the starting diene and dienophile moieties. For non-symmetrical monosubstituted dienes and dienophiles the preferential formation of isomers is usually observed. The transition state for 1,4-disubstituted dienes may be formed through *endo* or *exo* orientation of the reactants and thus two isomeric

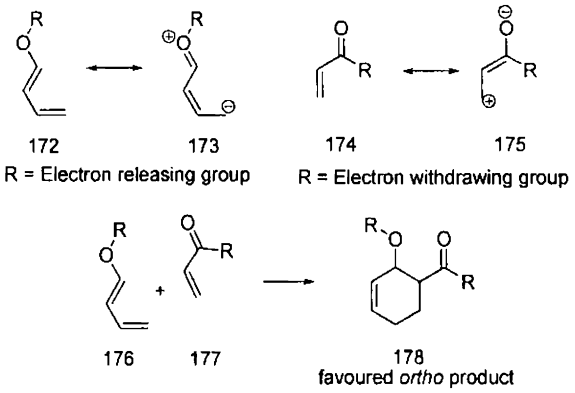
products could be produced. Typically, the *endo* transition state is favoured thus leading to the formation of respective *endo* adduct.



Scheme 39

In unsymmetrically substituted diene and dienophile, ortho and para orientations in products are usually favoured over meta orientation. A particular preference in location of substituents in the product can, in some cases, be explained in terms of frontier orbital theory. Most commonly, diene bears an electron-releasing group (ERG) and dienophile bears an electron-withdrawing group (EWG). The strongest interaction takes place between HOMO of diene and LUMO of dienophile. Carbons that have the highest coefficients in two frontier orbitals will begin to bond; therefore these carbons will direct the orientation of substituents and thus determine the major product of a DA reaction.

Dealing with the actual frontier orbital coefficients can be avoided since the preferred orientation in product can be described in terms of partial positive and negative charges that exist in diene and dienophile. Carbon with a partial negative charge will interact most readily with carbon bearing a partial positive charge. Therefore those two carbons will start coming together, thus dictating the relative orientation of substituents. The existence of partial positive/negative charge can always be determined by drawing resonance contributors for diene and dienophile, taking their ERG and EWG into consideration.



Scheme 40

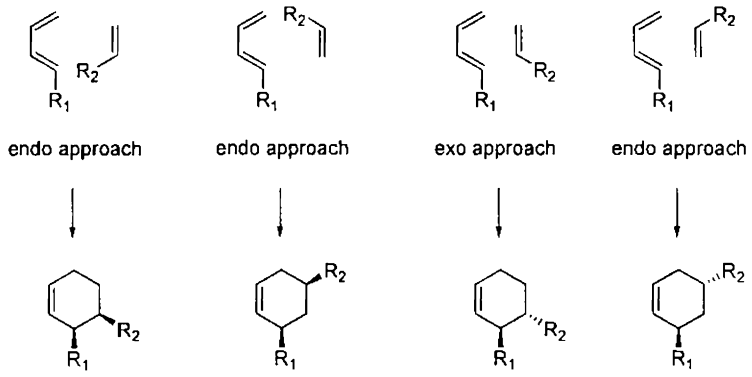
According to the 'cis principle' formulated by Alder and Stein in 1937, the stereochemistry of substituents in the starting material is retained in the product. This means that if a *cis*-dienophile is reacted, both of the *cis*-substituents will end up on same side (face) of the product ring. *trans*-Dienophile will yield a product where both of *trans*-substituents (that came originally from the dienophile) will be on different sides of the product ring. The same principle applies to dienes. *trans,trans*-1,4-Substituents will end up on same side of the ring, whereas *trans,cis*-1,4-substituents will be oriented towards different faces of the ring.

Besides the ortho/meta/para-forming orientations, the diene and dienophile may arrange themselves in different ways to yield *exo* and *endo* transition states which result in different products. To determine which is the *endo* and which is the exo transition state, the two molecules are oriented parallel to each other, such that diene's single bond (one which connects two double bonds) is parallel to dienophile's double or triple bond. It makes no difference whether the dienophile is positioned above or below the diene. The single substituent (or *cis*-substituents on the dienophile) is oriented to point in the directon of diene's π-system. This is the endo transition state (pictured below). If these substituents are pointed away from the diene, this would be the exo transition state.

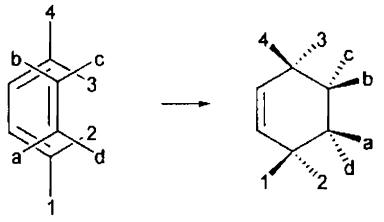
Using the 'cis principle' it is understood that *cis*-substituents on dienophile, for example, will end up on same side of the molecule. It is not obvious where the substituents on both diene and dienophile will end up relative to each other. To predict the orientation of these substituents that are coming from different molecules the different transition states have to be examined. The most stable transition state will lead to the major product. Transition state will also dictate the relative orientation of diene's and dienophile's substituents on the product ring. In some cases another rule can be applied: the 'endo addition rule'. According to this rule, the most stable transition state results when there is a 'maximum accumulation of double bonds'. This rule is not always followed. It has most application when dealing with cyclic dienes and dienophiles. For example, DA reaction of cyclopentadiene and maleic anhydride yields over 95% of the endo product.

It is important to note that labels "*exo*" and "endo" relate to the orientation of substituents in the transition state and not to a specific orientation of substituents in the product molecule. In each individual case,

the transition state has to be examined to see the most favoured relative orientation of substituents. It is not the case that for *endo* transition state the substituents on dienophile and 1,4-substituents on diene always point towards the same side of the newly formed ring. "*Endo*" and "*exo*" define specific transition states, not orientation of substituents. In the picture below, it just happens that the *endo* transition state will yield substituents on same side of the ring. This is not always so. In case of maleic anhydride and cyclopentadiene the *endo* product will have the R groups of diene and dienophile oriented toward the opposite sides of the newly formed ring.



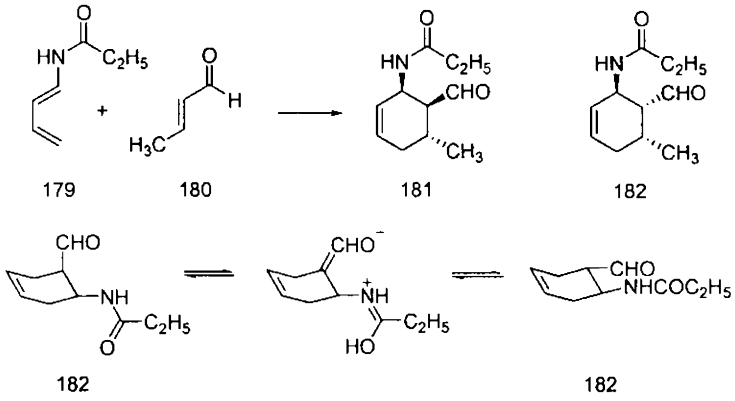
Scheme 41



Scheme 42

Exo product can predominate, however, for some reactions. This can happen when the resulting *endo* product can easily dissociate back into the starting material. In such reactions, *exo* product predominates over extended reaction times because *exo* product is thermodynamically favoured. In other

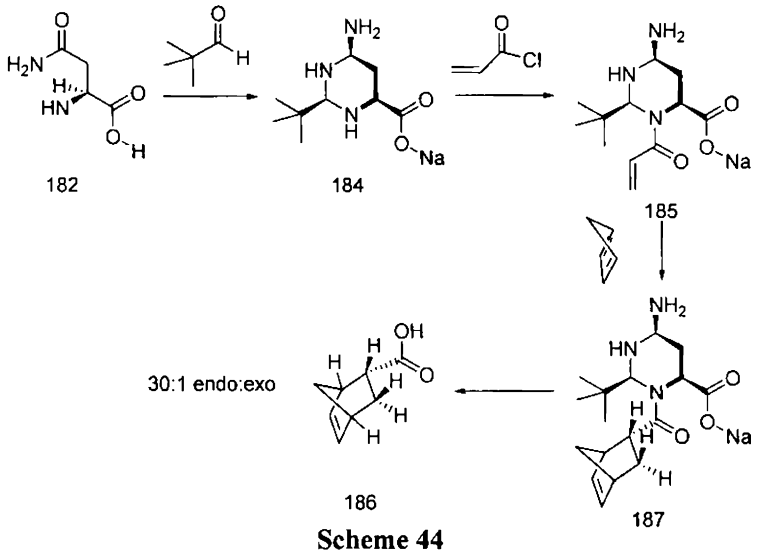
cases, *endo* product can convert to what would be the *exo* product of the reaction. In the example below, *endo* product **181** was the only one isolated after Diels-Alder reaction. However, letting the reaction go for prolonged periods of time yielded substantial amounts of *exo* product **182**. The authors speculated that *endo* product **181** can epimerise to *exo* product **182** in the following way:



Scheme 43

In summary, diastereoselectivity is based on the geometry of the most favoured transition state. For any given DA reaction, one can imagine one possible transition state being favoured over the other due to steric, stereoelectronic, and complexing factors. Thus, predictions can be made on the identity of major product of a particular DA reaction by looking at the starting material available.

Diels-Alder reactions lend themselves to chiral synthesis with chiral auxiliaries or chiral ligands. In one research effort,[304] the auxiliary is derived from L-asparagine. The telescopic synthesis with cyclopentadiene and acrylic acid yields the DA adduct with three stereocenters as predominantly the *endo* conformer (**184**) and with 54% *ee*.



Scheme 44

Lewis acids ($AlCl_3$, $ZnCl_2$, and others) act as catalysts by coordinating to the dienophile. The complexed dienophile becomes more electrophilic and more reactive toward the diene. This increases the rate and often the stereoselectivity of a DA reaction.

The asymmetric hetero-Diels-Alder (HDA) reaction is among the most powerful available methodologies for the construction of optically active six-membered heterocycles, with extensive synthetic applications in natural or unnatural products with a wide range of biological activity.[305] The DA reaction has high regioselectivity and *endo*-stereoselectivity. Some of the examples presented here use organocatalysis, which is a rapidly growing research field.[306]

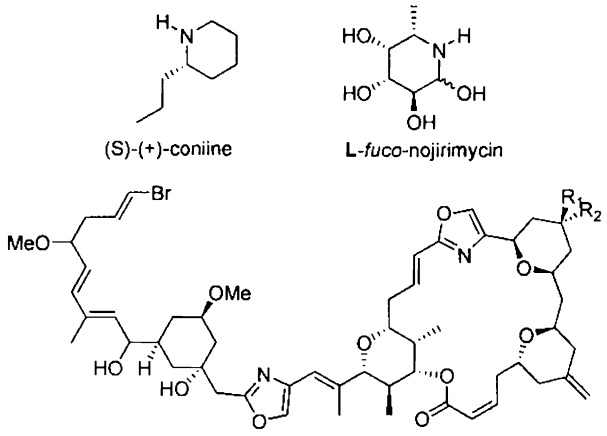
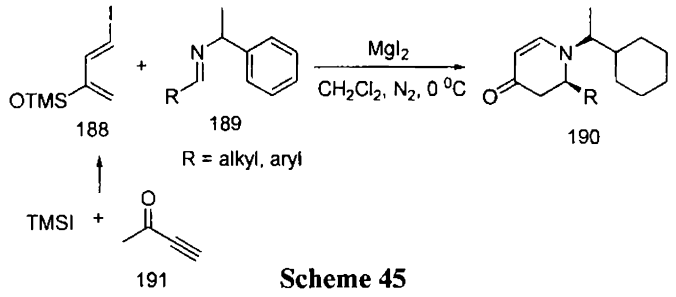


Chart 3

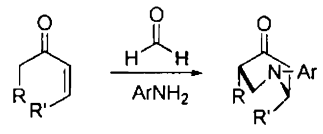
Timmons and coworkers[307] reported the first *aza*-DA reaction using a new class of iododiene **188** and chiral imines **289.** The methodology was used in the synthesis of dihydropyridones **190** (61-85% yield).



Scheme 45

Córdova and coworkers[308] reported the first one-pot three-component direct catalytic enantioselective *aza*-DA reaction. Synthetic viability of this reaction was tested using different ketones **192** (40-90% yield, 94-99% *ee*), formaldehyde and anilines (20-70% yield, 96-99% *ee*) in the presence of (*S*)-proline. The reaction occurs via a transition state in which the *in situ*-generated imine attacks the *si* face of the proline-derived catalyst. The

reaction is simple, can be performed in wet solvents, and is environmentally friendly.

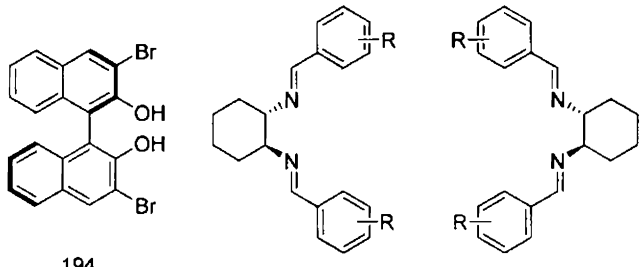


192 193

Ar = Ph, 3-OMe-C_6H_4, 4-Cl-C_6H_4

Scheme 46

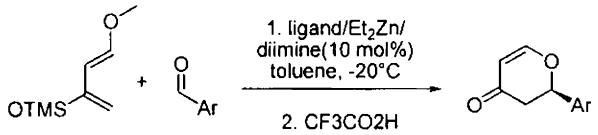
Ding and coworkers[309] successfully developed a catalytic *oxo*-DA reaction for the synthesis of 2,3-dihydro-4*H*-pyran-4-one derivatives **198** in excellent yields and high enantioselectivity. The authors used chiral zinc catalysts containing ligand **194**, various diimine activators (the best results were obtained using **195** and **196**), Danishefsky's-type diene **197** and aromatic aldehydes through a combinatorial approach(Scheme 47, Chart 4).



194 195 196

R = 4-Cl, 3-OMe R = 4-Br, 2,6-Cl_2

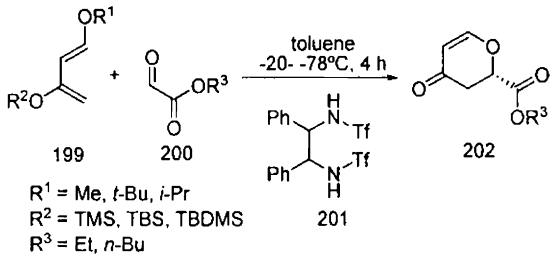
Chart 4



197 198

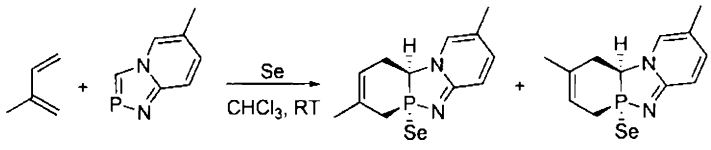
Scheme 47

Using chiral lanthanide complexes with (*R,R*)-DPENTf (**201**), Tonoi and Mikami[310] report a catalytic *oxo*-DA reaction between Danishefsky's-type diene **199** and glyoxylate **200** (23-87% yield, 23-86% *ee*). The reaction proceeds through double hydrogen bonding using bis-triflylamide as chiral Brønsted acid catalyst (Scheme 48).



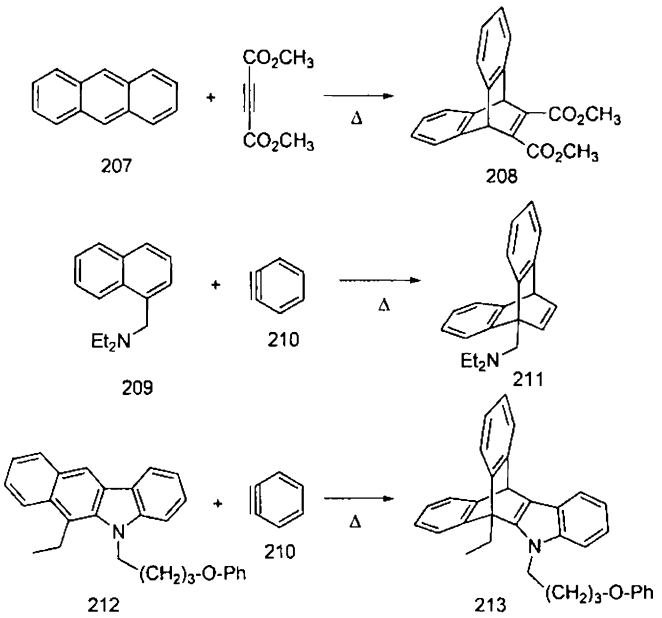
Scheme 48

Kumawat and coworkers[311] developed a regioselective (4:1 *de*, 50% yield) hetero Diels-Alder (HDA) reaction between isoprene (**203**) and [1,4,2]diazaphospholo[4,5-*a*]pyridines (**204**) in the presence of selenium (Scheme 49). The weaker C=P π-bond (relative to the C=C π-bond), lowers the activation energy needed for the cyclisation and favours the HDA reaction.

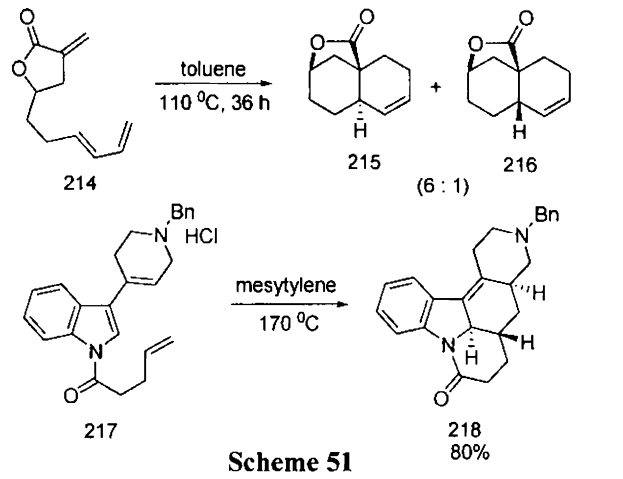


Scheme 49

A number of polycyclic aromatic hydrocarbons react with dienophiles by 1,4-addition, but the reaction is particularly characteristic of anthracenes and the higher linear acenes[312-313] (Scheme 50).



Scheme 50



Scheme 51

Intramolecular Diels Alder reaction between unsymmetrically substituted dienes and dienophiles usually show regioselectivity. Given below are a few examples in which the synthetic utility of intramolecular Diels-Alder reactions is revealed[314-316] (Scheme 51).

With myriad applications, often as a crucial element in elegant and programmed cascade sequences facilitating the construction of complex molecules, the Diels-Alder cycloaddition has afforded numerous and unparalleled solutions to a diverse range of synthetic puzzles provided by nature in the form of natural products. Ever since its discovery, development continued with no let up in pace. Its application not only leads to a strong increase in molecular complexity (molecular size, topology, stereochemistry, functionality, and appendages), but also can result in structures that lend themselves to additional amplification of complexity by the use of other powerful synthetic reactions.

1.8. Michael-Type Additions

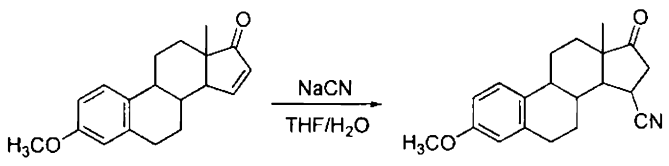
Addition reactions proceed *via* a variety of mechanisms. Among the various mechanistic possibilities, nucleophilic addition to electron deficient olefins is probably the most important. As originally defined by Michael,[317] the reaction is the addition of an enolate of a ketone or aldehyde to an α,β-unsaturated carbonyl compound at the β carbon. A newer definition, proposed by Kohler,[318] is the 1,4-addition of a doubly stabilized carbon nucleophile to an α,β-unsaturated carbonyl compound. Some examples of nucleophiles include β-ketoesters, malonates, and β-cyanoesters. The resulting product contains a highly useful 1,5-dioxygenated pattern. Here the nucleophile is termed as "donor" and the electron deficient olefin is regarded as the "acceptor". Active methylenes, amines, alcohols, and thiols are common donors and electron deficient olefins such as α,β-unsaturated carbonyl compounds, nitriles and nitro compounds are common acceptors. With certain donors, a base is required to promote the reaction. When the donor is a carbanion (or an enolate ion), and the reaction results in the formation of a

new C-C bond, it is termed as Michael addition. With all other donors, the reaction is collectively expressed as Michael-type addition.

Michael addition of carbon nucleophiles to electron deficient olefins is a classical and fundamental carbon–carbon bond-forming reaction.[319] This reaction and its close variants have been extensively used in organic synthesis.[320] Generally, Michael additions are conducted in a suitable solvent in the presence of a strong base either at room temperature or at elevated temperatures.[321] Due to the presence of the strong base, side reactions such as multiple condensations, polymerisations, rearrangements and *retro*-Michael additions are common. These undesirable side reactions decrease the yields of the target adduct and render their purification difficult. Better results can be obtained by employing weaker bases such as piperidine, quaternary ammonium hydroxide, tertiary amines etc.[322] There have been some reports on Michael reactions catalysed by potassium carbonate in organic solvents,[232] and water in the presence of surfactants[324] or phase-transfer catalysts.[325] To a large extent, mild bases restrain the formation of side products, thus improving the yield of the desired Michael adducts. Recently, non-conventional procedures like conducting the reaction on the surface of a dry medium[326] or under microwave irradiation[327] were found to facilitate the Michael reaction. For the purposes of eco-friendly "green chemistry", a reaction should ideally, be conducted under solvent-free conditions with minimal or no side-product formation and with utmost atom economy.[328]

Classical examples of the Michael addition reaction include reaction between diethyl malonate (Michael acceptor) and diethyl fumarate, mesityloxide and diethyl malonate, diethyl malonate and methyl crotonate, 2-nitropropane and methyl acrylate, phenyl cyanoacetate and acrylonitrile, and nitropropane and methyl vinyl ketone.[329-333]

The Michael addition is an important atom-economical method for diastereoselective and enantioselective C-C bond formation. A classical tandem sequence of Michael and aldol additions is the Robinson annulation. More recent research has focused on expanding the scope of asymmetric Michael additions. The most common methods involve chiral phase transfer catalysis, involving chiral quaternary ammonium salts derived from the Cinchona alkaloids, and organocatalysis, which uses enamine or iminium activation with chiral secondary amines, usually derived from proline. A more dramatic example of Michael addition is illustrated in the transformation that constituted the first step in a multi-step synthesis of the steroid estron[334] (**220**) (Scheme 52).



219 220

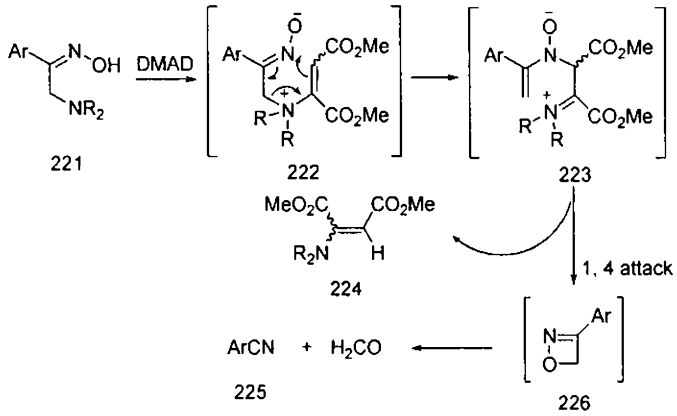
Scheme 52

Addition of nucleophilic species including amines, alcohols to electron deficient double bonds holds tremendous application potential and utility in organic synthesis.[335] Particularly, addition of amines to α,β-unsaturated carbonyl compounds and nitriles produce β-amino derivatives which are useful intermediates in the synthesis of a large number of products with a wide range of biological activity.[2] Similarly, nucleophiles such as amines and alcohols readily add to electron deficient acetylenes.

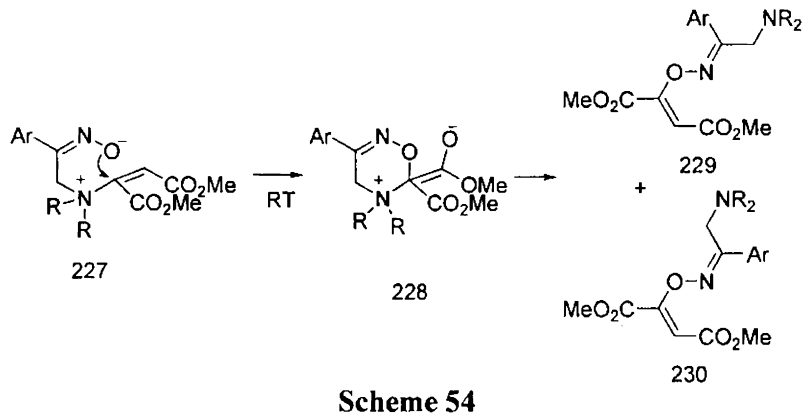
Reactivity between primary, secondary, and tertiary amines and ethyl 3-cyanoacrylate (ECA) exhibit significant differences. Tertiary amines initiate rapid ECA polymerisation with a strong exotherm to produce high molecular weight polymers. In contrast, the reaction of ECA with primary or secondary

amines occurs at a much slower rate resulting in low molecular weight oligomers or polymers. Based on ^{1}H NMR and IR spectroscopic study, it was demonstrated that intramolecular proton transfer occurs after the initial Michael-type addition of the primary or the secondary amine to the ECA double bond to form aminocyanopropionate esters. The differences in reactivity among the three classes of amines with ECA can be attributed to the initial formation of aminocyanopropionate esters for primary and secondary amines and only polymer for tertiary amines.[322b] However, a few subtle differences here deserve special mention. Bergmann's review[337] shows that acetylenic acceptors sometimes add two molecules of donors or the initial product often cyclise. The tendency of the initial Michael adducts to cyclise has been utilized to construct numerous heterocyclic compounds.[338]

Coskun and Arikan[339] reported the rearrangement of adducts from α-dialkylaminoketone oximes **221** and DMAD in acetonitrile at reflux leading to benzonitrile and dialkylaminomaleate probably *via* an unstable 4*H*-1,2-oxazete **226** (Scheme 53) and the formation of 2-(2-dialkylamino-1-phenylethylideneaminooxy)-but-2-enedioic acid dimethyl esters **229** and **230** (Scheme 54) when the reaction is performed at room temperature.

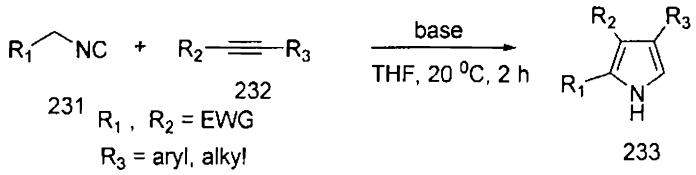


Scheme 53



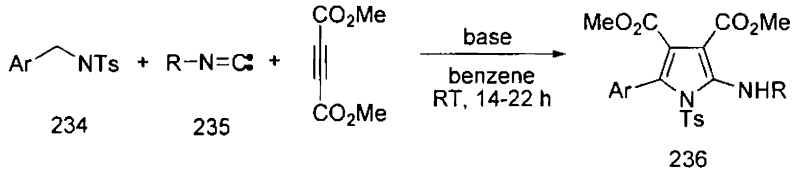
Scheme 54

Various 2,3,4-trisubstituted pyrroles are easily synthesised in one step from readily available acetylenes and acceptor-substituted methyl isocyanides by base-mediated or copper-catalysed cycloadditions that are taking place *via* Michael-type additions.[340]



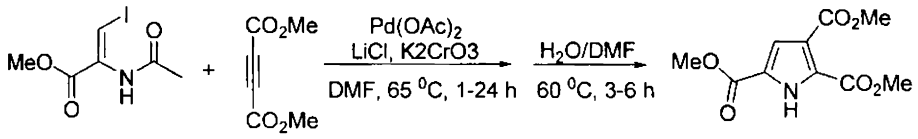
Scheme 55

Several novel and efficient multicomponent reactions leading to 2-aminopyrroles are also reported which involves a Michael-type addition as a key step. In the reaction of *N*-tosylimines, DMAD, and isocyanides, the isocyanate first adds to DMAD in a Michael-type fashion which is followed by the imine attack in the reaction.[341]



Scheme 56

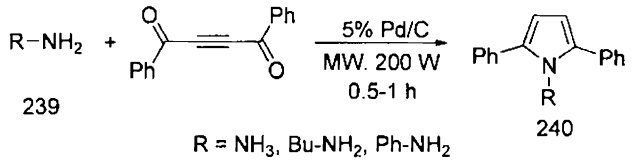
An efficient and regioselective palladium-catalysed cyclisation of internal alkynes and 2-amino-3-iodoacrylates **237** have shown to substituted highly-functionalised pyrroles **238** in good yields.[342]



237 238

Scheme 57

A convenient microwave-assisted one pot-reaction from but-2-ene-1,4-diones and but-2-yne-1,4-diones *via* Pd/C-catalysed hydrogenation of the carbon-carbon double bond/triple bond followed by amination-cyclisation yields several aryl-substituted pyrrole derivates.[343]



239 240

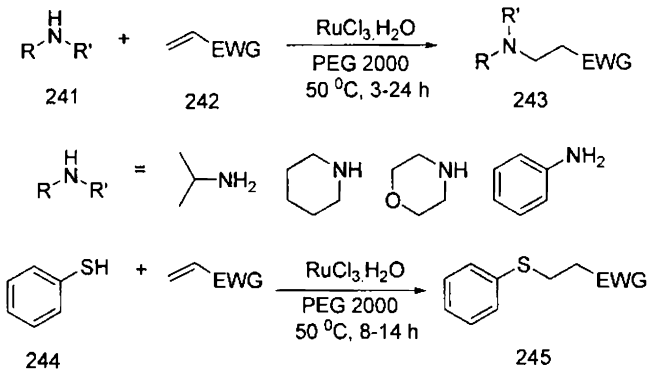
R = NH_3, Bu-NH_2, Ph-NH_2

Scheme 58

A versatile $RuCl_3$-catalyzed 1,4-conjugate addition of primary, secondary and aromatic amines, thiols, and carbamate to α,β-unsaturated compounds in poly(ethylene glycol) (PEG) provides the desired β-substituted carbonyls in high yields. Its properties of low sensitivity toward moisture and oxygen, high tolerance of different functional groups, and efficient recyclability make $RuCl_3$-PEG suitable for both laboratory and industrial scale synthesis of β-substituted carbonyls.[344]

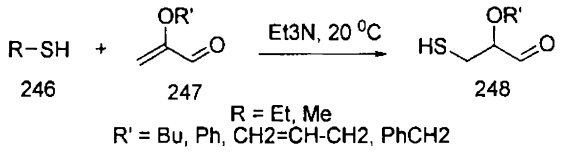
Michael-type addition (conjugate addition reaction between electron-poor olefins and nucleophiles, such as thiols) has been successfully used as a convenient tool for surface fictionalisation. Due to its mild character, this method is potentially useful for the introduction of sensitive groups, which can

provide bioactivity and targeting possibilities to surfaces of, for example, colloidal carriers. Michael-type reactions, using thiols, possibly present in peptidic structures, and acrylates, at the end of protein-repellent PEG chains have also been illustrated. Satisfactory results were obtained with thiols in solution and acrylic groups bound to the surface. Alternatively, the use of thiols on the particles, even if generated in situ, did not provide useful results.



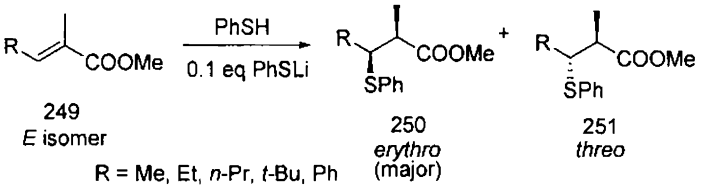
Scheme 59

Several 1,4-addition reactions of mercaptans[345] and thiophenol[346] to α,β-unsaturated aldehydes proceed readily in the absence of a catalyst at room temperature and also in the presence of tertiary amines (triethylamine, piperidine) giving rise to the formation of 1,4-addition products.[346-349] Addition reaction of alkanethiols to 2-chloro-2-butenal in the presence of potassium carbonate at 80 °C follows the same 1,4-addition pattern.[350] Reaction of 2-alkoxypropenals with organothiols in the presence of small amounts of a base was shown to yield 3-organosulphanyl-2-alkoxypropanals.



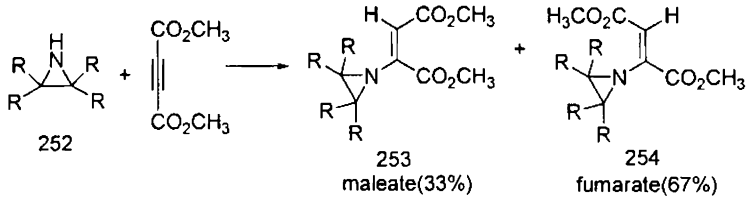
Scheme 60

The stereochemistry of nucleophilic addition of thiophenol to α,β-unsaturated esters has not been well investigated except only a few cases.[352] Miyata and coworkers[353] carried out the addition of thiophenol to an electron-deficient olefin using a pair of α,β-unsaturated esters with *E* and *Z* geometry, methyl tiglate *E*-(1) and methyl angelicate *Z*-(4), in the presence of base. Quantitative results were obtained in all cases giving the adducts with the ratio (*erythro/threo*) of 94:6, showing preferential formation of the *erythro*-adduct.



Scheme 61

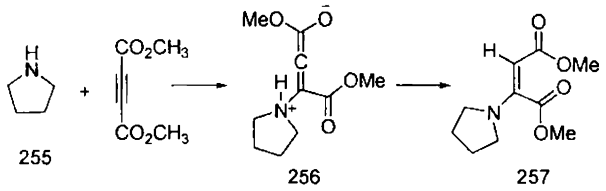
With acetylenes, depending on the nature of solvents employed and reaction conditions, addition reaction can either be 'cis' or 'trans' yielding the *E* and *Z*-isomers of the corresponding olefin products. For example, both cis and trans addition of amines to various acetylenes have been reported.[354] Aziridines (**252**) add to DMAD in methanol to give 67% fumarate **254** and 33% maleate **253**.



Scheme 62

In protic solvents such as methanol, solvation of the incipient Michael anion is very efficient. In the Michael-type addition reactions of several heterocyclic amine donors[355] with acetylenes, the imine or iminium ion[356]

intermediates are involved. In contrast to the stereochemical outcome observed with aziridines, with most other heterocyclic bases, the *E*-isomer is either predominantly or exclusively formed. In most cases, overall stereochemical outcome is decided by thermodynamic control. Secondary amines, for example, add 'cis' to dimethyl acetylenedicarboxylate (DMAD) to give the corresponding maleates.

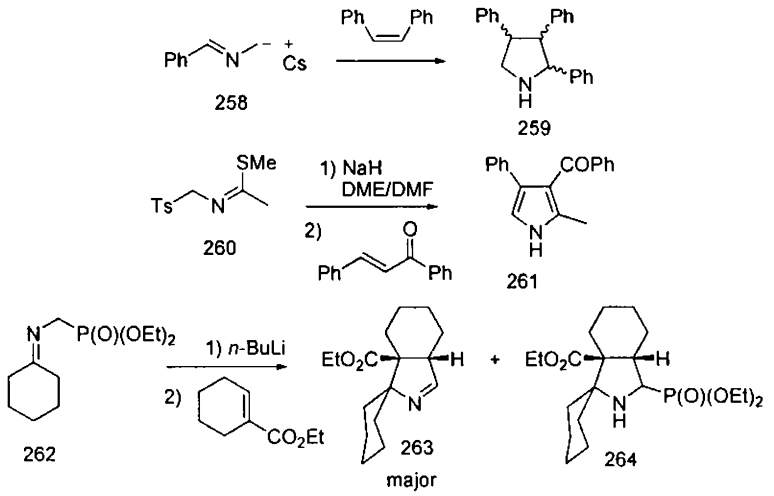


Scheme 63

It may be noted that steric crowding is less with maleates (*E*-isomers) than with fumarates (*Z*-isomers). However, caution should be applied while predicting the initial stereochemical outcome of amine addition to DMAD by observing the stereochemistry of the product isolated from these reactions. It has independently been established that such fumarates readily isomerise to give the corresponding maleates. Protic solvents accelerate the isomerisation process.[357] Thus it is quite probable that the initially formed fumarates equilibrate to give the more stable maleates. Similarly, alcohols also add cis to DMAD in presence of tertiary amines as catalyst.

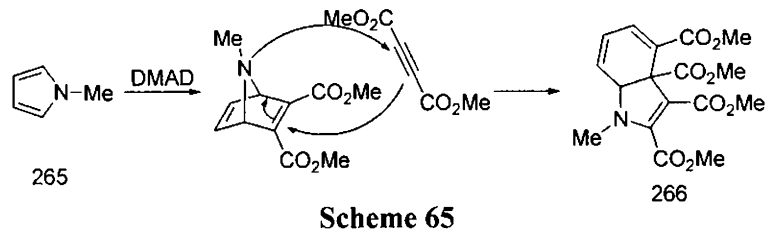
The interaction of 1-phenyl-2-azaallyl anion with electron-poor alkenes has also been studied by these researchers[358-359] as well as the group of Achiwa,[360-361] largely giving Michael addition rather than cycloaddition products, although an example of the latter does exist.[359] Tsuge and Kanemasa[358] have generated the 1-phenyl-2-azaallyl anion **258** and used it in cycloadditions with stilbenes and styrene. Stabilised 2-azaallyl anions, i.e. those bearing anion-stabilizing groups such as CN, CO_2R, $P(O)(OR)_2$, etc.,

have been generated by the deprotonation of imines and have been reported in many laboratories to undergo [π4s+π2s] cycloadditions, typically with electron-poor alkenes.[362-365]



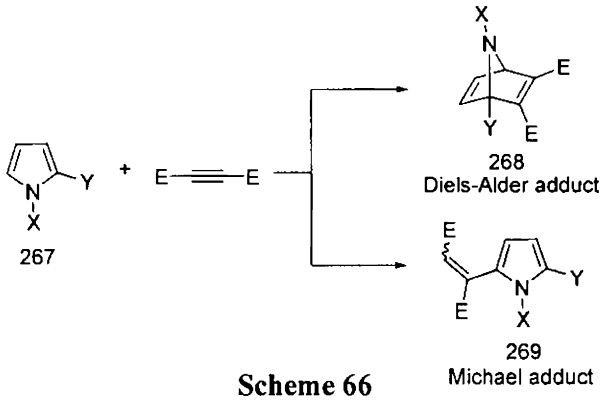
Scheme 64

The predominance of pathway between cycloaddition and Michael-type addition depends upon the substrate and the Michael acceptor. For the reaction of pyrroles with DMAD, Diels and Alder isolated an unusual 2:1 adduct from the reaction of dimethyl acetylenedicarboxylate (DMAD) and *N*-methylpyrrole **265,** but were unable to deduce the structure.[366a] Acheson and Vernon eventually identified the 2:1 adduct as **266** and suggested that this substance is formed from an intermediate 1:1 adduct via a cyclic mechanism (Scheme 65).[366b] This reaction is an early example of the aza-Claisen family of [3,3] sigmatropic shifts.



Scheme 65

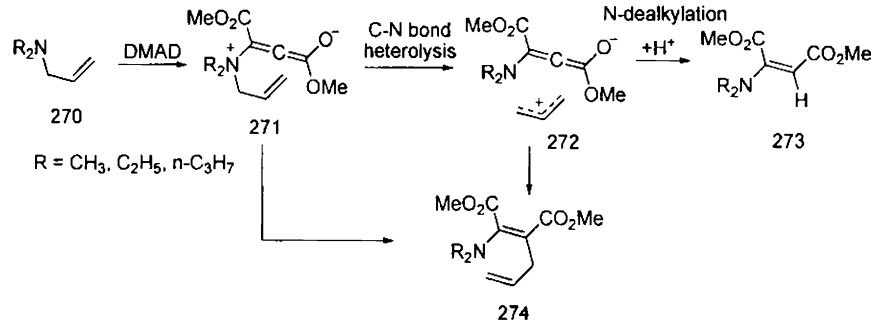
Thus reactions of substituted pyrroles with electron deficient acetylenes usually follow two different pathways: a) a Diels-Alder reaction of the pyrrole ring at both of its positions (C2/C5) or b) a Michael-type addition to one of its positions (C2 or C5) to yield a vinyl substituted pyrrole.[367] The specific outcome of the reaction is strongly dependent on the substituent at the nitrogen atom. *N*-substituted pyrroles bearing aryl or electron withdrawing groups at nitrogen atom will facilitate a [4+2] cycloaddition.[366] In contrast when the *N*-substituent is alkyl group, as in 1-methylpyrrole, the bicyclic 1:2 adduct is the resulting product in the reaction. This was explained by Acheson and Vernon[3] through the initial formation of a Michael adduct which then reacts with a second molecule of DMAD to yield the 1:2 adduct. Through *ab initio* studies, the mechanism of both the reaction pathways has shown to be taking place through the initial Michael-type addition of DMAD which then leads to the formation of either the substituted fumarate/maleate or the Diels-Alder adduct, thus following a stepwise mechanism.[368]



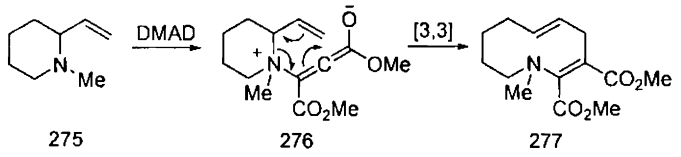
Scheme 66

Many related rearrangements involving addition of allylic amines to acetylenic esters are now known, and recent papers by Kandeel and Vernon[369] and by Schwan and Warkentin[370] have explored the thermal reaction in depth. Mariano and coworkers have used analogous reactions of propiolate esters

with allylic amines in alkaloid synthesis,[371] and several other groups have also made valuable contribution.[372] To quickly summarize this data (Scheme 66), the [3,3] rearrangement to **274** can take place by the equivalent of a cyclic transition state or by an ionic pathway involving C-N bond heterolysis to the ion pair **272** and recombination to **274**. Depending on the conditions, **271** may decompose by enolate *C*-protonation or by nucleophilic capture of the cation, resulting in net *N*-dealkylation and the formation of **273**. If the allylic fragment has additional substitution, then the cation can also decompose by elimination reaction.[372]



Scheme 67



Scheme 68

1.9. Outline of the Research Problem and its Importance

Barrelenes are well known for their interesting photochemical transformations in high yields exhibiting remarkable selectivity based on the nature of excited states involved. Our interest was in the study on the control over these pathways through selective quenching of either the singlet or triplet excited state and thereby improving the yield of a desired product of choice.

In this perspective we targeted the synthesis of a dibenzobarrelene system designed to have suitable built-in singlet quencher components, which may selectively and efficiently quench the singlet excited states of these molecules in an intramolecular fashion. The dibenzobarrelenes of our choice had an inbuilt 'donor-spacer-acceptor' geometry that facilitate intramolecular quenching of excited states by electron transfer while enriching the triplet excited state population. We selected tertiary amine components as potential singlet quenchers based on the premise that tertiary amines quench singlet excited states through electron transfer. We zeroed in on the Diels-Alder reactions of (anthracen-9-yl)methylamines with a reactive dienophile like dimethyl acetylenedicarboxylate (DMAD) for the synthesis of the dibenzobarrelenes of our choice. However, Diels-Alder reaction of (anthracen-9-yl)methylamines with DMAD failed to generate target bicyclic compounds in productive yields. Instead, different unexpected products were formed in these reactions. Dramatic solvent dependence was observed in these reactions. We encountered interesting observations in these reactions based on 'donor-acceptor' interactions such as electron transfer reactions taking place between the tertiary amine and acetylenes leading to bond dissociations, electron transfer mediated nucleophilic substitution reactions, Michael-type addition reactions and Diels-Alder reactions. Our attempts to unravel the chemistry behind these interesting tranformations made us to undertake a detailed study of pathways and mechanisms of these solvent dependent reactions. A thorough understanding of ground state and excited state electron transfer reactions of amines and anthracenes will help in an improved understanding of the solvent dependent reactions undergone by them. In this context, we were interested in examining the factors that the influence the reactions such as:

1. Nature of amine moiety based on structural features including, steric and electronic environment: We designed several (anthracen-9-yl)methylamines and the selection of the structural features were based on the criterion that the tertiary amine in substrate had variable steric and electronic environment thereby tuning the electron donating capacity.

2. Nature of acetylenes based on structure and reactivity. The observed electron transfer reactions and nucleophilic addition reactions would depend on the nature of the acetylene employed. We proposed to study the reaction using acetylenes of varying reactivity.

3. Nature of solvent: a) polarity - nonpolar, polar aprotic, polar protic nature, b) Brønstead acidity, and c) viscosity.

4. Effect of reaction temperature and reaction time on competing reactions.

5. Extension of the studies on sulphur analogues: As an extension to our present studies we decided to explore the mechanistic possibilities of solvent dependent reactions in sulphur analogues: (Anthracen-9-yl)methylsulphanes.

1.10. The objectives of the present work:

1. Investigations on the reaction between (anthracen-9-yl)methylamines and acetylenes

   a) Recognise the ideal structural features of (anthracen-9-yl)methylamines suitable for donor-acceptor type reactions and synthesise them in quality and quantity required for various reactions.

b) Understand the role of nature of solvent in the reaction by carrying out the reaction in solvents formalised in non-polar-polar aprotic-polar protic range.

c) Find the effect of temperature, time and atmosphere on the reaction.

d) Study the influence of nature of acetylene in the reaction.

2. Extension of the studies on sulphur analogues - (Anthracen-9-yl)methylsulphanes

   Design and synthesise a few (anthracen-9-yl)methylsulphanes and to study their solvent dependent reactions with acetylenes.

3. Explore the interesting photoinitiated electron transfer reactions in (anthracen-9-yl)methylamines.

   Study the effect of steric and electronic environment of the tertiary amine on the PET quenching of (anthracen-9-yl)methylamines by studying the fluorescence emission spectrum. Study the decay kinetics using time correlated single photon counting technique (TCSPC) and derive the quantum yield, rate constant and free energy associated with electron transfer reactions in the excited state and correlate results with the structural aspects.

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Chapter - 2

SYNTHESIS OF (ANTHRACEN-9-YL)METHYLAMINES

2.1. Abstract

This chapter deals with our endeavours on the synthesis of several (anthracen-9-yl)methylamines that would serve as potential substrates for the study of competing electron transfer, Michael type addition and Diels-Alder reactions with suitable electron deficient acetylenes. These molecules are of great interest due to their significant photophysical and photochemical behaviour as well. We employed Leuckart Reaction and nucleophilic substitution to access the required (anthracen-9-yl)methylamines.

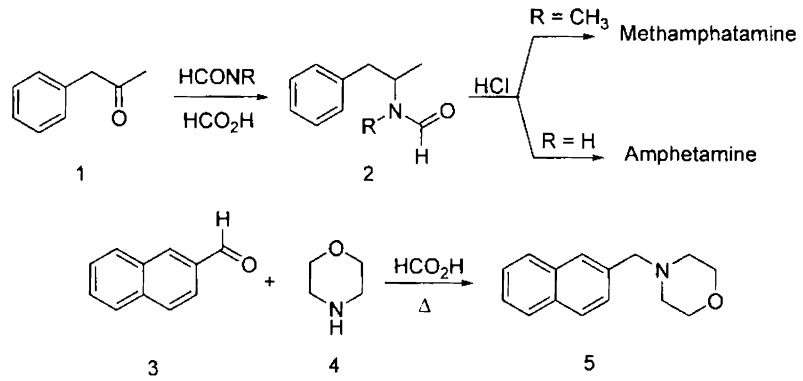
2.2. Introduction

We have examined several substrates with the potential to undergo competing electron transfer, Michael type addition and Diels-Alder reactions with suitable substrates. Anthracenes are excellent dienes and are known to undergo Diels-Alder reaction with a variety of dienophiles. Tertiary amines are known to undergo single electron transfer, which make them important in several electrochemical[1-3], photochemical[4-14] and biochemical[15-18] redox processes. Radical cations of amines are principal intermediates in a large number of electron transfer reactions and are involved in the synthesis of amino acids, alkaloids and several other nitrogen-containing compounds of biological and pharmaceutical importance. Tertiary amines can participate as

Michael donors in their reactions with electron deficient acetylenes. The ideal system for the present study has a tertiary amine component linked to an anthracene ring through a spacer. The anthracene component in the compounds can undergo Diels-Alder reaction whereas the amine component electron transfer and Michael-type addition reactions with suitable acetylenes. The methylene spacer will effectively shut the electronic communication between arene and anthracene components in the ground state.

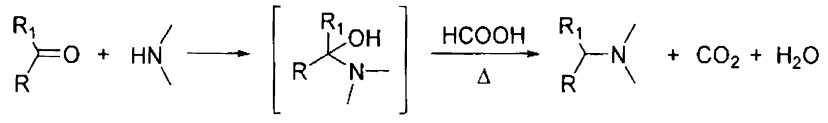
In this chapter, we converge on the synthetic routes to the required amine-appended anthracene compounds. We employed Leuckart reaction[19] and simple nucleophilic substitution reactions on suitable halides to synthesise the target compounds. A brief overview of these methods is presented in the following paragraphs.

Leuckart reaction, discovered in 1885, is best known for the reductive alkylation of ammonia and amines, in which formic acid or a derivative thereof serves as the reducing agent. Some examples of this reaction are shown below (Scheme 1). Leuckart synthesis has been widely exploited in laboratory in the early and mid 1970's and was the popular clandestine route to amphetamine and methamphetamine. Several literature references link the Leuckart synthesis (Scheme 1) to methamphetamine[20-22] and amphetamine[23-25].



Scheme 1

The mechanism of Leuckart reaction has been studied.[26-28] The final reduction step is shown to be a free radical process initiated by formic acid. A general mechanism[21] is given in Scheme 2. The reaction proceeds with a variety of sunbstrates and the required amines are generated in high yields.

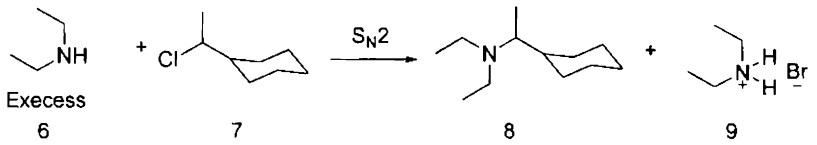


Scheme 2

In 1956, E. Marcus and J. T. Fitzpatrick[29] reported an extension of Leuckart reaction in the synthesis of dimethylaminomethyl derivatives of pyrene, perylene, anthracene and naphthalene. Following this lead, we synthesised a few of our target molecules by the reductive aminoalkylation of 9-formylanthracene.

Ammonia and many amines are excellent nucleophiles that bond to and form products with a variety of electrophiles. Some of the electrophiles that are known to react with amines are alkyl halides, alkyl sulphonates, aldehydes or ketones, acid halide or anhydride, sulphonyl chloride, nitrous acid etc. A typical amination reaction proceeding through an S_N2 process is indicated in

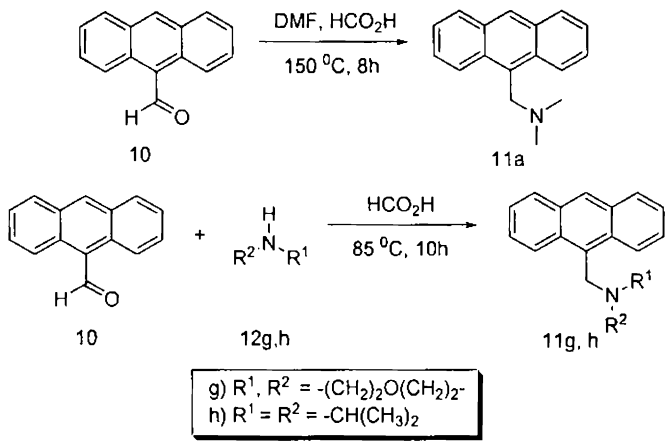
Scheme 3. We adopted this method to prepare several amine-appended anthracenes by the reaction between suitable secondary amines and 9-chloromethylanthracene.



Scheme 3

2.3. Results and Discussion

We employed Leuckart reaction for the synthesis of 9-(*N,N*-dimethyl-aminomethyl)anthracene[29](**11a**), 9-(*N,N*-diisopropylaminomethyl)anthracene[30] (**11g**), and *N*-(anthracen-9-yl)methylmorpholine[31] (**11h**) (Scheme 4).

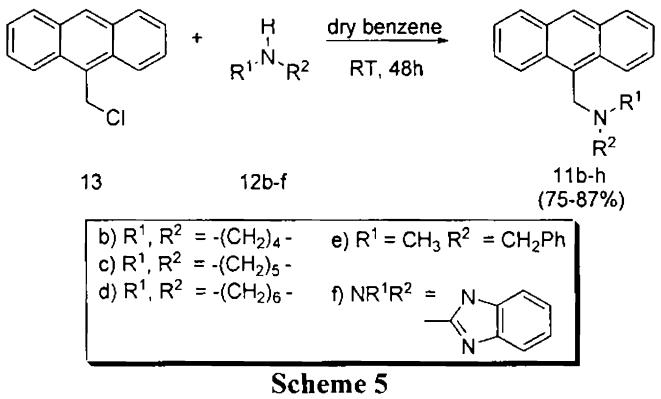


Scheme 4

A neat reaction under reflux using 9-anthraldehyde with the corresponding secondary amine **12g,h** in presence of formic acid afforded the required (anthracen-9-yl)methylamines. The residue obtained upon removal of excess secondary amine and formic acid was suspended in diethyl ether. Passing gaseous hydrogen chloride to saturation resulted in the precipitation of

11g,h as the corresponding hydrochlorides. The hydrochloride salt obtained was treated with saturated solution of $NaHCO_3$ and extracted with diethyl ether to obtain **11g,h** in excellent yields (86-90%). For the preparation of **11a,** a slight modification to of Leuckart reaction was employed using 9-anthraldehyde and *N,N*-dimethylformamide (DMF) in presence of formic acid. It was found that using slight excess of formic acid resulted in better yields in the above reaction.

Nucleophilic substitution on 9-chloromethylanthracene (**13**) with suitable secondary amines **12b-f** yielded (anthracen-9-yl)methylamines **11b-f**. We employed secondary amines such as pyrrolidine (**12b**), piperidine (**12c**), azepine (**12d**), *N*-methylbenzylamine (**12e**) and 2-methylbenzimidazole (**12f**) to obtain the corresponding derivatives **11b-f** (Scheme 5). When dry tetrahydrofuran (THF) was used as the solvent the reaction took place inefficiently and the products were obtained in poor yields. Better yields (75-87%) were obtained when benzene was used as solvent in all the cases.



Scheme 5

9-Chloromethylanthracene was freshly generated by the reaction of thionyl chloride ($SOCl_2$) with 9-anthracenemethanol in dry benzene at room temperature (RT) for 1.5 hours and then heating at 80 ^{0}C for half and hour. Upon removal of excess thionyl chloride and benzene under reduced pressure,

yellow crystals of **13** were formed. Fresh solvent was added along with 2 equivalents of the secondary amine and the reaction mixture was kept stirring for 48 hours. Progress of the reaction was followed through thin layer chromatography (TLC).

Analytically pure sample of **11a-h** (Chart 1) were obtained by recrystallisation from hexane/dichloromethane mixture. The UV spectra of all these compounds were similar and were dominated by the absorption of the anthracene component. ^{1}H NMR spectra of all these compounds were comparable with those reported in literature and they exhibited acceptable elemental analysis and mass spectral data. Based on these data, the compounds were confirmed as (anthracen-9-yl)methylamines **11a-h**.

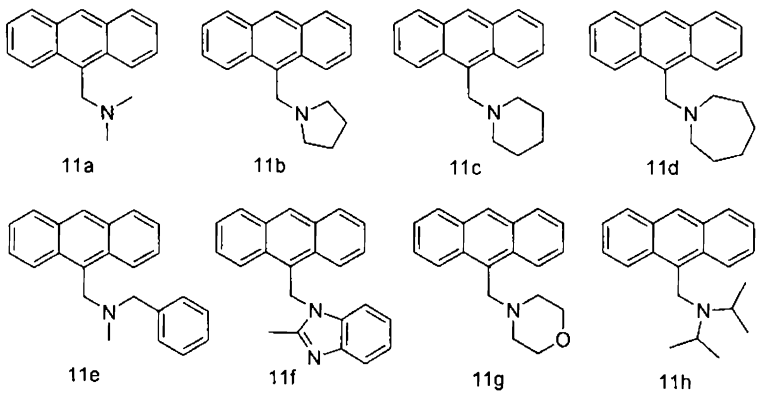


Chart 1

Thus, we synthesised several (anthracen-9-yl)methylamines, with an aim to examine their reactivity towards acetylenic dienophiles in different solvents which is discussed in the following chapters. Besides, (anthracen-9-yl)methylamines are well known for their photoinitiated electron transfer reactions. Preliminary findings on the photophysical behaviour of these molecules are compiled in Chapter 3.

2.4. Experimental

2.4.1. General Procedures.

All melting points are uncorrected and were determined on a Neolab melting point apparatus. All reactions and chromatographic separations were monitored by thin layer chromatography (TLC). Glass plates coated with dried and activated silica gel or aluminium sheets coated with silica gel (Merck) were used for thin layer chromatography. Visualisation was achieved by exposure to iodine vapours or UV radiation. Column chromatography was carried out with slurry-packed silica gel (Qualigens, 60-120 mesh). Absorption spectra were recorded using Shimadzu 160A spectrometer and infrared spectra were recorded using ABB Bomem (MB Series) FT-IR spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded at 300, 400 and 500 MHz on Bruker FT-NMR spectrometers with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in parts per million (ppm) downfield of TMS. Elemental analysis was performed using Elementar Systeme (Vario ELIII) and GC-MS analysis was performed using Varian 2000 L Single Quadrupole instrument. We have reported only the relevant data for the characterisation of novel compounds synthesised by us.

2.4.2. Starting Materials. All standard reagents were purchased from S. D. Fine Chem. Ltd. and were used as obtained. Solvents were distilled and dried as per requirements.

2.4.2.1. 9-Anthraldehyde: 9-Anthraldehyde was prepared using a known procedure[32] (54%, mp 104-106 ^{0}C).

2.4.2.2. 9-Anthracenemethanol: 9-Anthracenemethanol was prepared using a known procedure[33] (60%, mp 158-162 ^{0}C).

2.4.2.3. 9-Chloromethylanthracene: 9-Chloromethylanthracene was prepared by a known method[33] (84%, mp 136-138 ^{0}C).

2.4.3. Preparation of (Anthracen-9-yl)methylamines

2.4.3.1. Preparation of 9-(*N,N*-Dimethylaminomethyl)anthracene (11a).

To a solution of 9-anthraldehyde (3.0 g, 15 mmol) in 15 mL of dry DMF, formic acid (0.8 mL of 90% solution) was added and the mixture was stirred under reflux for 6 h. Excess solvent was removed by distillation under reduced pressure and the residual oil was dissolved in ether and filtered. Hydrogen chloride gas was passed through the ether solution to precipitate the hydrochloride of 9-(*N,N*-dimethylaminomethyl)anthracene (3.0 g) which was filtered and washed with ether. The hydrochloride obtained was treated with saturated solution of $NaHCO_3$ and extracted with ether. The ether extract was dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressure and the solid obtained was recrystallised from a mixture (1:3) of hexane and dichloromethane to separate pure **11a**.

Compound 11a: (86%); mp 66-68[34] ^{0}C; UV λ_{max} (methanol) 255 nm (ε 42000), 365 nm (ε 1000); ^{1}H NMR ($CDCl_3$) δ 2.23 (6H, s), 4.32 (2H, s), 7.49-8.55 (9H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 45.05, 54.31, 124.97, 125.04, 125.60, 127.03, 128.71, 130.44, 130.61, 130.97; MS, *m/z* 235 (M^+), and other peaks; Anal. Calcd for $C_{17}H_{17}N$: C, 86.77; H, 7.28; N, 5.95; Found: C, 86.78; H, 7.27; N, 5.95.

2.4.3.2. Preparation of *N*-((Anthracen-9-yl)methyl)pyrrolidine[35] (11b).

To a solution of 9-chloromethylanthracene (2.50 g, 11 mmol) in 10 mL of dry benzene, pyrrolidine (1.57 g, 22 mmol) was added and stirred at RT for 24 h. The reaction mixture was poured into water and extracted with diethyl ether to

remove pyrrolidine hydrochloride formed as a side product. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the solid obtained (2.36 g) was recrystallised from a mixture (1:3) of hexane and dichloromethane to give pure **11b**.

Compound 11b: (82%); mp 108-110 ^{0}C; UV λ_{max} (acetonitrile) 255nm (ε 63000), 365 nm (ε 2100); ^{1}H NMR ($CDCl_3$) δ 1.61-1.89 (4H, m), 2.82-3.07 (4H, m), 4.62 (2H, s), 7.51-8.54 (9H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 26.95, 53.70, 54.71, 124.51, 125.08, 125.13, 126.96, 128.62, 131.13, 131.21; MS, *m/z* 261 (M^+), and other peaks; Anal. Calcd for $C_{19}H_{19}N$: C, 87.31; H, 7.33; N, 5.36; Found: C, 87.25; H, 7.38; N, 5.40.

When the reaction was conducted in dry THF, a complex mixture of products was obtained along with **11b**.

2.4.3.3. Preparation of *N*-((Anthracen-9-yl)methyl)piperidine[36] (11c).

To a solution of 9-chloromethylanthracene (2.50 g, 11 mmol) in 10 mL of dry benzene, piperidine (1.88 g, 22 mmol) was added and stirred at RT for 24 h. The reaction mixture was poured into water and extracted with diethyl ether to remove piperidine hydrochloride formed as a side product. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the solid obtained (2.43 g) was recrystallised from a mixture of (1:3) hexane and dichloromethane to separate pure **11c**.

Compound 11c: (80%); mp 119-121 ^{0}C; UV λ_{max} (methanol) 255 nm (ε 72000), 365 nm (ε 3700); ^{1}H NMR ($CDCl_3$) δ 1.52-1.76 (6H, m), 2.60-2.82 (4H, m), 4.54 (2H, s), 7.52-8.59 (9H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 24.24, 25.83, 54.45, 54.77, 124.51, 125.04, 125.16, 126.99, 128.61, 131.18,

131.25; MS, *m/z* 275 (M^+), and other peaks; Anal. Calcd for $C_{20}H_{21}N$: C, 87.23; H, 7.69; N, 5.09; Found: C, 87.24; H, 7.67; N, 5.09.

2.4.3.4. Preparation of *N*-((Anthracen-9-yl)methyl)hexamethyleneimine (11d).

To a solution of 9-chloromethylanthracene (2.50 g, 11 mmol) in 10mL of dry benzene, 2 eq. of hexamethyleneimine (2.19 g, 22 mmol) was added and stirred at RT for 24 h. The reaction mixture was poured into water and extracted with diethyl ether to remove hexamethyleneimine hydrochloride formed as a side product. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the solid obtained (2.78 g) was recrystallised from a mixture (1:3) of hexane and dichloromethane to separate pure **11d**.

Compound 11d: (87%); mp 102-104 ^{0}C; UV λ_{max} (methanol) 255 nm (ε 56000), 365 nm (ε 1400); ^{1}H NMR ($CDCl_3$) δ 1.77-1.80 (6H, m), 2.70 (6H, m), 4.62 (2H, s), 7.46-8.58 (9H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 23.67, 25.72, 51.43, 54.36, 124.84, 125.09, 125.54, 127.18, 130.96, 131.20, 131.53; MS, *m/z* 289 (M^+), and other peaks; Anal. Calcd for $C_{21}H_{23}N$: C, 87.15; H, 8.01; N, 4.84; Found: C, 87.16; H, 8.01; N, 4.83.

2.4.3.5. Preparation of 9-(*N*-Methyl-*N*-benzylaminomethyl)anthracene (11e).

To a solution of 9-chloromethylanthracene (2.50 g, 11 mmol) in 10 mL of dry benzene, 2 eq. of *N*-methylbenzylamine (2.67 g, 22 mmol) was added and stirred at RT for 24 h. The reaction mixture was poured into water and extracted with diethyl ether to remove *N*-methylbenzylamine: hydrochloride formed as a side product. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. Solvent was removed under reduced

pressure and the solid obtained (2.89 g) was recrystallised from a mixture (1:2) of hexane and dichloromethane to separate pure **11e**.

Compound 11e: (84%); mp 116-118 ^{0}C; UV λ_{max} (methanol) 255 nm (ε 47000), 366 nm (ε 2200); ^{1}H NMR ($CDCl_3$) δ 2.28 (2H, s), 3.74 (2H, s), 4.53 (2H, s), 7.28-8.54 (14H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 42.18, 53.63, 62.50, 124.83, 125.13, 125.59, 127.04, 127.49, 128.19, 129.01, 130.43, 131.39, 131.48, 139.44; MS, *m/z* 311 (M^+), and other peaks; Anal; Calcd for $C_{23}H_{21}N$: C, 88.71; H, 6.80; N, 4.50; Found: C, 88.75; H, 6.78; N, 4.47.

2.4.3.6. Preparation of 1-((Anthracen-9-yl)methyl)-2-methyl-1*H*-benzo[*d*]-imidazole (11f).

To a solution of 9-chloromethylanthracene (2.50 g, 11 mmol) in 10 mL of dry benzene, 2 eq. of 2-methyl benzimidazole (2.89 g, 22 mmol) was added and stirred at RT for 24 h. The reaction mixture was poured into water and extracted with diethyl ether to remove the piperidine: hydrochloride formed as a side product. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the solid obtained (2.81 g) was recrystallised from a mixture (1:4) of hexane and dichloromethane to separate pure **11f**.

Compound 11f: (79%); mp 100-102 ^{0}C; UV λ_{max} (methanol) 255nm (ε 53000), 365 nm (ε 1600); ^{1}H NMR ($CDCl_3$) δ 2.31 (3H, s), 6.16 (2H, s), 6.82-8.58 (14H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 15.37, 42.02, 109.85, 119.08, 121.73, 122.14, 123.11, 124.66, 125.29, 127.31, 129.50, 129.63, 131.07, 131.31, 142.55, 152.06; MS, *m/z* 322 (M^+), and other peaks; Anal. Calcd for $C_{23}H_{18}N_2$: C, 85.68; H, 5.63; N, 8.69; Found: C, 85.71; H, 5.67; N, 8.62.

2.4.3.7. Preparation of *N*-((Anthracen-9-yl)methyl)morpholine (11g).

Formic acid (2.76 g, 60 mmol) was mixed with 20 mL of morpholine at RT and the mixture was rapidly cooled in a water bath. To this, 9-anthraldehyde (2.50 g, 12 mmol) was added and the mixture was heated at 80 ^{0}C. Rapid evolution of carbon dioxide was observed. After the evolution stopped, the solution was refluxed for 8 h. The reaction mixture was poured into water and extracted with diethyl ether. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the solid obtained was passed through a silica plug to remove unchanged 9-anthraldehyde (<5%) using a mixture (1:1) of hexane and dichloromethane. The product was washed using a mixture (1:9) of ethyl acetate and dichloromethane. The yellow solid obtained (3.03 g) upon removal of solvent was recrystallised from a mixture (1:3) of hexane and dichloromethane to separate pure **11g**.

Compound 11g: (90%); mp 122-124 ^{0}C; UV λ_{max} (methanol) 255 nm (ε 60000), 365 nm (ε 2300); ^{1}H NMR ($CDCl_3$) δ 2.65 (4H, m), 3.67-3.74 (4H, m), 4.48 (2H, s), 7.47-8.52 (9H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 53.70, 54.59, 67.15, 124.89, 125.03, 125.69, 127.62, 129.01, 131.40, 131.44; MS, *m/z* 277 (M^+), and other peaks; Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05; Found: C, 82.29; H, 6.86; N, 5.01.

2.4.3.8. Preparation of 9-(*N,N*-Diisopropylaminomethyl)anthracene (11h).

Formic acid (2.76 g, 60 mmol) was mixed with 20 mL of *N,N*-diisopropylamine at RT and the mixture was rapidly cooled in a water bath. To this, 9-anthraldehyde (2.50 g, 12 mmol) was added and the flask was heated at 80 ^{0}C. Rapid evolution of carbon dioxide was observed. After the evolution stops the solution was refluxed for 10 h. The reaction mixture was poured into water and extracted with diethyl ether. The organic layer was

separated, washed with water, and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the solid obtained was passed through a silica plug to remove unchanged 9-anthraldehyde (10%) using a mixture (1:1) of hexane and dichloromethane. The product was washed out using a mixture (1:9) of ethyl acetate and dichloromethane. The yellow solid obtained (3.02g) upon removal of solvent was recrystallised from a mixture (1:4) of hexane and dichloromethane to separate pure **11h**.

Compound 11h: (85%); mp 129-132[30] ^{0}C; UV λ_{max} (methanol) 255nm (ε 50000), 365 nm (ε 1100); ^{1}H NMR ($CDCl_3$) δ 1.15-1.17 (6H, d, J = 8.8 Hz), 2.96-3.05 (2H, m), 4.67 (2H, s), 7.44-8.73 (9H, m, aromatic); ^{13}C NMR ($CDCl_3$) δ 21.05, 41.47, 46.71, 124.80, 125.04, 125.41, 127.05, 131.55, 131.77, 131.89; MS, *m/z* 291 *(M^+)*, and other peaks; Anal. Calcd for $C_{21}H_{25}N$: C, 86.55; H, 8.65; N, 4.81; Found: C, 86.54; H, 8.66; N, 4.80.

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Chapter - 3

PREILIMINARY PHOTOPHYSICAL INVESTIGATIONS ON (ANTHRACEN-9-YL)METHYLAMINES

3.1. Abstract

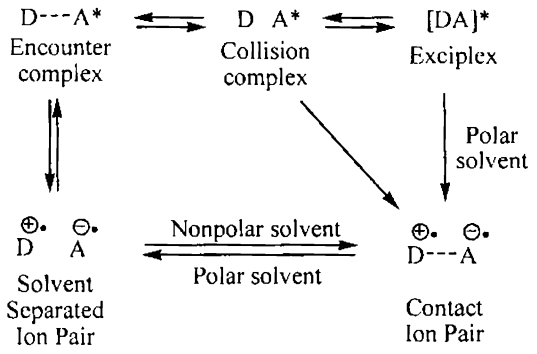
This chapter deals with the preliminary photophysical studies on the (anthracen-9-yl)methylamines synthesised by us. Analysis of absorption and the fluorescence emission spectra of these compounds showed the presence of intramolecular Photo-initiated Electron Transfer (PET) leading to quenching of excited states, the efficiency of which depends on geometrical constraints and electronic factors pertaining to the molecule. The decay kinetics studied using Time Correlated Single Photon Counting (TCSPC) showed a bi-exponential decay indicating the involvement of two transient species in the excited state of these molecules.

3.2. Introduction

Photodriven supramolecular systems[1] are useful for information gathering, storing, processing and transmission.[2-4] Molecules that perform logic operations are prerequisites for molecular information processing and computations.[5-15] Several researchers have reported receptor molecules that can be considered to perform simple logical operations by coupling ionic bonding or more complex molecular recognition processes with photoionic (fluorescence) signals.[16-20] In such systems a chemical binding will result in change in fluorescence intensity from the receptor molecule.

The development and study on such systems was mainly focussed on the phenomenon of photoinduced electron transfer (PET) in 'donor' – 'acceptor' type molecules.[16-17] The important goal of molecular arithmetic can be achieved in principle if 'off-on' digital[21] AND and XOR logic gates[22,23] with independent inputs are available to operate on binary numbers. There are interesting reports on their application in the signal processing, as fluorescence p*H* indicator[24] and as chemical[25] and biological[26] sensors.

Nanosecond and picosecond laser-flash photolysis techniques have been used by different groups to elucidate various intermediate stages involved in the photoinduced reactions of such systems.[27] The overall mechanism involving electron transfer process in a solvent medium is illustrated in Scheme 1.



Scheme 1

The dynamics of the process involve the formation of an encounter complex between the excited state molecule and the ground state molecule.[28-30] The encounter complex can be described as an intermolecular ensemble of excited and ground state molecules, separated by a small distance (*ca.* 7 Å) and surrounded by solvent molecules. During the lifetime of the encounter complex, the reactants undergo mutual collisions inside the solvent cage and as a result of these collisions, a stage is reached where the reactants

are in contact to form a 'collision complex'. If the interaction between the reactants is strong enough (*ca.* 5-20 kcalmol^{-1}), the collision complex can rapidly change to a new intermediate called exciplex, which has partial charge character and a large dipole moment. Electron transfer can occur at any of these stages.[28] Electron transfer from the collision complex or from the exciplex leads to the charge transfer species called a contact ion pair. The contact ion pair can undergo separation in the solvent cage to generate a solvent-separated ion pair. The solvent-separated ion pairs can then diffuse apart from the solvent cage and become separated to form the free solvated radical ions, which are analogous to free radicals and can undergo chemical reactions to yield products.

All these processes, *viz.* formation of the encounter complex, collision complex, contact ion pairs, solvent separated ion pairs, and free-radical ion pairs, are reversible. For generation of free radicals in good yields, forward electron transfer processes have to compete efficiently with the energy wasting back-electron transfer processes.[31]

Electron-transfer reactions of amines are important in several technological applications such as imaging, photopolymerisation and is also implied in the fading of textile dyes having amine functionality.[32-36] More recently electron donating capacity of amine functionality has been extensively used for designing new materials such as fluoroionophores, organic conductors, electroluminescent materials, photovoltaics, and materials with non-linear optical activity.[37-48] It has been reported that inter[49-51] and intramolecular[52-56] electron and energy transfer, exciplex formation[51] etc. take place between arenes and tertiary amines. The formation of intramolecular arene-amine exciplex and their photophysical and photochemical behaviour has been of longstanding interest.[2,5-20,50,57]

The mechanism of electron transfer reactions of amines has been studied by different methods, including the thermochemical, electrochemical, photochemical, and radiation chemical techniques. A widely studied technique in aminoalkylaromatic hydrocarbons is the photoinduced electron transfer (PET) quenching. Several PET sensor molecules are designed with modular structure 'fluorophore-spacer-receptor' format. A few of the molecules that are reported to be useful in florescence signalling are given in Chart 1.

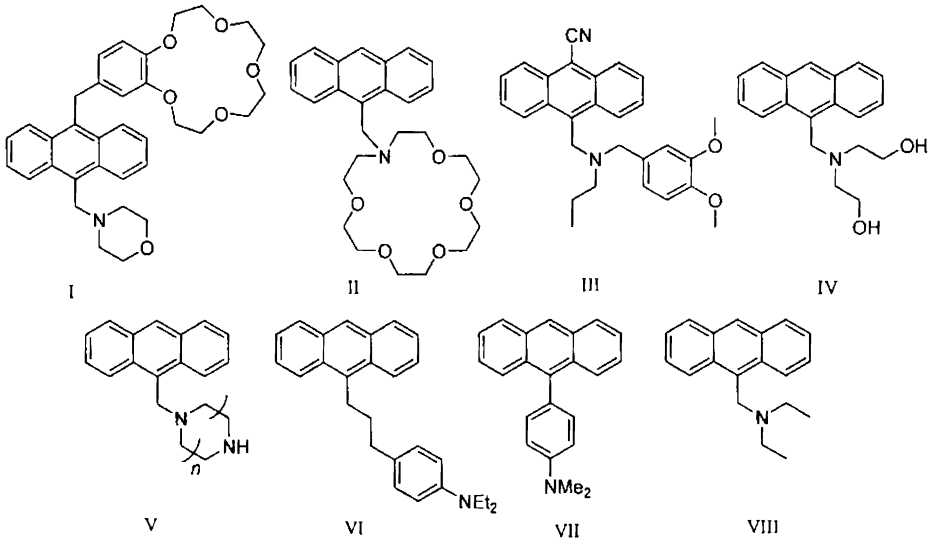


Chart 1

For systems with inbuilt amine-arene unit, the PET mechanism is shown to be taking place in the excited state by an initial single electron transfer from the tertiary amine to the arene moiety leading to an internal exciplex.[58,59] This is followed by a radiationless energy loss to form an internal radical ion pair. A back electron transfer thereby regenerates the ground state molecule. This quenching of anthracene fluorescence involving electron transfer correlates

with the redox potentials of the donor-acceptor pair. Alternatively triplet enrichment is a distinct possibility here.

The feasibility of electron transfer process can be predicted by considering free energy change associated it. Weller[60] derived a kinetic relationship for the redox potential differences to evaluate the ability of PET quenching to compete with other relaxation phenomenon. Comparisons of the reduction potential of the acceptor and oxidation potential of the donor can be used to determine the free energy change and the rate of transfer. Electron transfer is considered to be fast if this difference in the redox potentials is ≤ 0 V ($\Delta G^0 \leq 0$ kcalmol^{-1} and $k_{ET} \sim$ diffusion controlled).[61]

Exciplex formation and decay was found to be dependent on several factors, including: i) the redox properties of the amine donor and the arene acceptor moiety, ii) the chain length of the aliphatic bridge between them, iii) the point of attachment of the bridge onto the arene and iv) solvent polarity. Any interaction such as Lewis base coordination of the amine lone pair (e. g. protonation, metal chelation, complexation to cations) decreases its ability to quench fluorescence *via* PET, resulting in an observed chelation-enhanced fluorescence (CHEF). It has been reported that the solvent viscosity and dielectric properties (polarity) can affect the exciplex/excimer formation and electron transfer in different ways. Viscosity plays an important role in the excimer formation, but is not so important in electron transfer. Conversely a change in polarity has only a small effect on excimer formation.

Most of the cases studied consisted of systems with variable spacers and spacer lengths between the donor and acceptor.[60-63] Relevant work on the geometric requirements for exciplex formation in aminoalkylnaphthalenes has been reported by Chandross and Thomas[63] and by Davison and co-workers[58a,d,64] which reveals that benzylic amines are uniquely positioned

for efficient PET. Long tethers between donor and acceptor molecules result in a number of ground state configurations where the donor is not sufficiently near the acceptor, so that on excitation, several bond rotations must occur to allow proper alignment for electron transfer. Additionally they postulate that the efficient quenching for the benzylic case maybe a result of through bond interactions *via* C-C bonds of the methylene spacer. Beeson and co-wrokers[65] confirmed that the effectiveness of intramolecular quenching event decreases as the donor becomes more distal.

The (anthracen-9-yl)methylamines we have synthesised are benzylic analogues and consist of structural variable on ring size. These systems would be ideal for the study of dependence of geometric requirements of ring size, steric and electronic factors on exciplex formation and electron transfer in these systems. For such systems, knowledge of structural and geometrical relationship to PET would be useful in the design of several sensors relying on intramolecular amine PET, given that the greatest signal range will result from sensors with the lowest initial fluorescence. This chapter describes preliminary studies on the ground state and excited state interactions of these (anthracen-9-yl)methylamines keeping 9-methylanthracene as reference. We studied the excited states of the (anthracen-9-yl)methylamines *via* time-correlated single photon counting technique (TCSPC) and derived the life times of the transient species involved in the excited states. Interesting results are obtained which are discussed in the paragraphs below.

3.3. Results and Discussion

(Anthracen-9-yl)methylamines **1a-h** synthesised by us have inbuilt amine-arene unit with tertiary amine components possessing varying steric and electronic makeup (Chart 2). The absorption spectra and the fluorescence emission spectra (λ_{ex} = 364 nm) of **1a-h** were recorded in methanol (10^{-5} M) at

room temperature. Time-resolved studies were conducted using TCSPC technique using methanol as solvent.

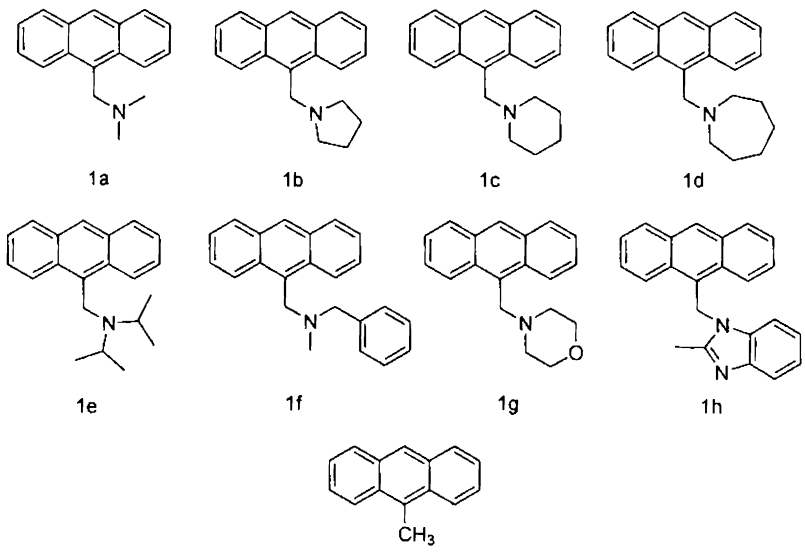


Chart 2

The absorption spectra of amine-appended anthracenes **1a-h** were almost identical with that of 9-methylanthracene (**2**) indicating negligible ground state interaction between anthracene and amine components (Figure 1). Excitation spectrum of **1a-h** resembled the absorbance spectrum indicating the emission is taking place from the locally excited state (Figure 2).

Fluorescence emission spectra of **1a-h** showed a slight red shift (1-7 nm) in comparison to **2** owing to perturbation due to substituent effects. For **1a-h** considerable quenching of anthracene fluorescence (29-99%) was observed (Table 1). Compounds **1f** and **1g** showed high efficiency in quenching (99 and 98% respectively). This was followed by **1e** (94%), and the cyclic amines **1a-d** (90, 90, 88, 82% respectively). Among the series, **1h** showed least efficiency (28%) in quenching of anthracene fluorescence.

It is interesting to note that the fluorescence quenching capability of compounds **1a-d** is in the decreasing order of the size of *N*-substituent with **1a** as the one with least geometrical constraint. Compound **1d**, which has a seven membered ring showed the least efficiency (82%) in quenching among the **1a-d** series. This shows that as the ring size increase on the donor atom efficiency for intramolecular quenching via PET is reduced. This may be due to the fact that the efficiency of electron transfer from the amine lone pair to the anthracene component depends largely on the steric deformations of the amine nonbonding orbital.

Table 1. PET Quenching in **1a-h**

Molecule	% Quenching (Compared to **2**)	λ_{em}, nm
1a	90	416
1b	90	418
1c	88	417
1d	82	417
1e	94	417
1f	99	411
1g	98	415
1h	28	413

Compound **1e**, which has a strong basic amine component, shows higher quenching capability when compared to **1a-d** series in spite of its bulky nature. Effect of electron availability on nitrogen is further demonstrated by the observation in **1h** where the nitrogen is a part of an aromatic ring system like benzimidazole.

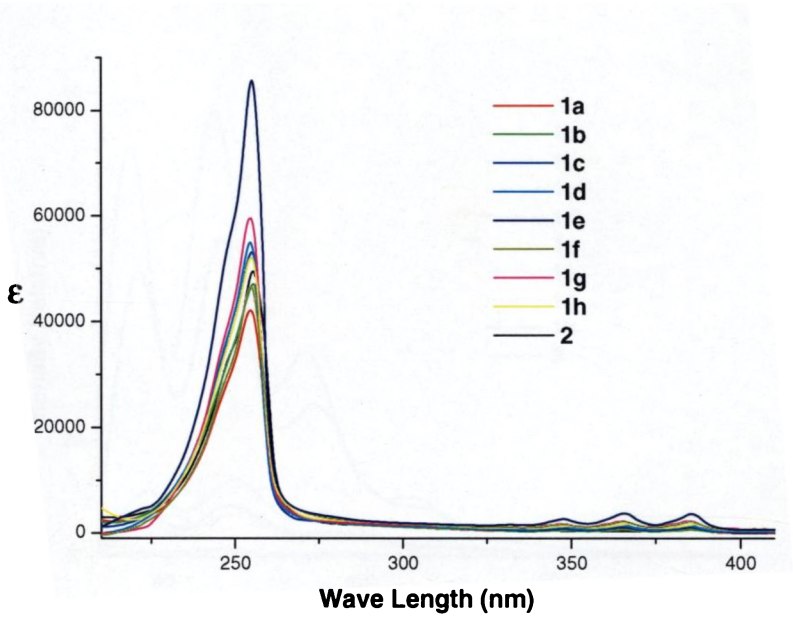


Figure 1. Absorption spectra of **1a-e** and **2** at RT in 10^{-5} M methanol

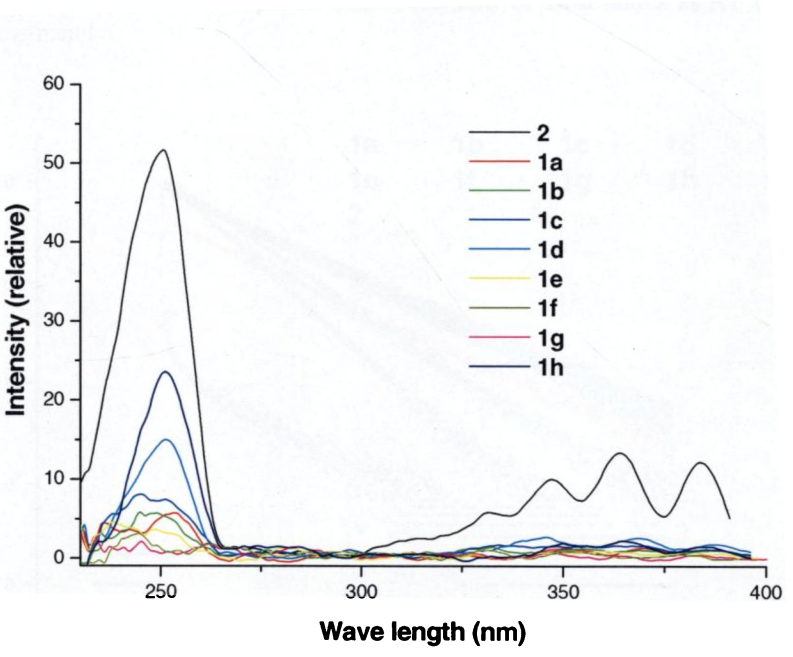


Figure 2. Excitation spectra (λ_{em} = 365 nm) of **1a-h** and **2** at RT in 10^{-5} M methanol

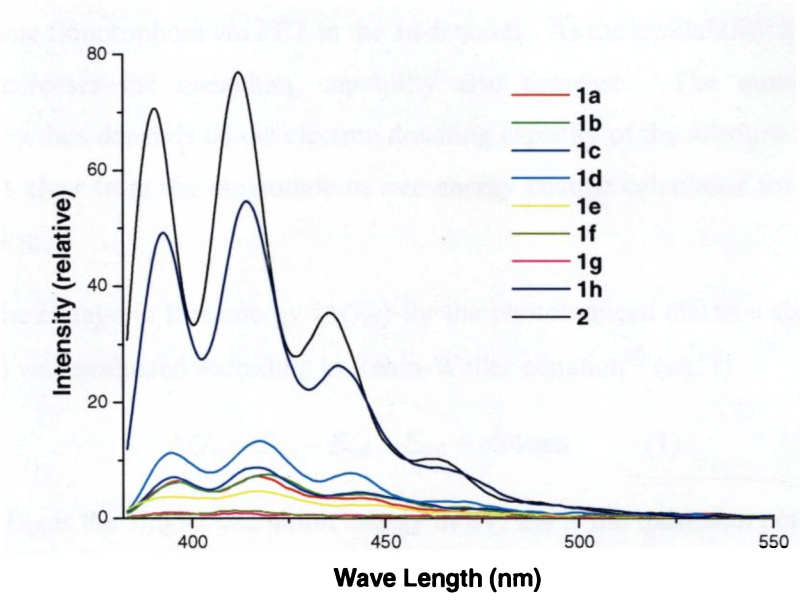


Figure 3. Fluorescence emission spectra (λ_{ex} = 365 nm) of **1a-h** and **2** at RT in 10^{-5} M methanol

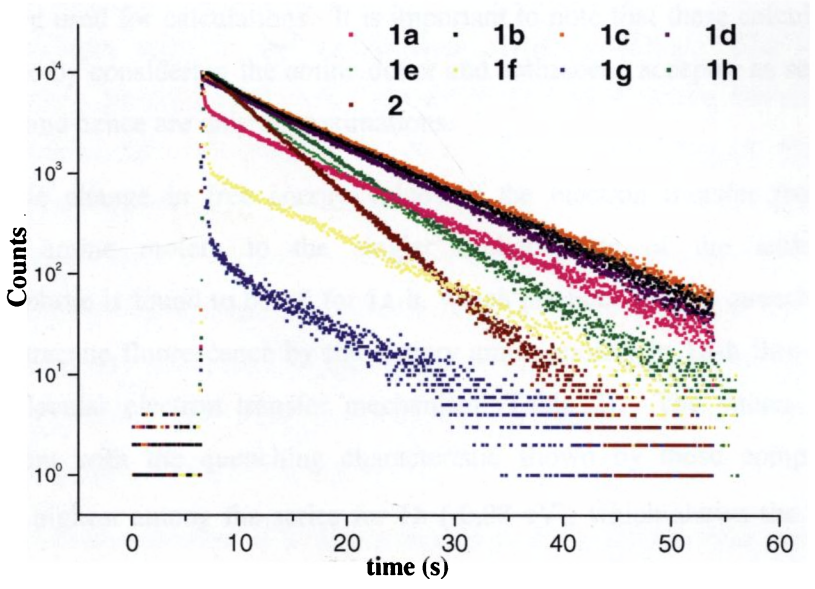


Figure 4. Decay curves of **1a-h** and **2** in 10^{-5} M methanol

Compound **1h** showed the least magnitude of fluorescence quenching of anthracene flouorophore *via* PET in the **1a-h** series. As the availability of lone pairs decreases the quenching capability also decrease. The quenching efficiency thus depends on the electron donating capacity of the nitrogen atom, which is clear from the magnitude in free energy change calculated for these molecules.

The change in free energy (ΔG_{ET}) for the photoinduced electron transfer reaction was evaluated according to Rehm-Weller equation[60] (eq. 1)

$$\Delta G_{ET} = E_{ox} - E_{red} - E_{0,0} + e^2/4\pi\varepsilon d \qquad (1)$$

where, $E_{0,0}$ is the singlet excitation energy in eV, E_{ox} is the oxidation potential of the donor and E_{red} is the reduction potential of the acceptor, ε is the dielectric constant of the solvent and d is the distance between donor and acceptor. Oxidation potential of **1a-h** were taken from literature. Reduction potential (-1.97 eV)[66], and singlet state energy of 9-methylanthracene (3.21 eV) were used for calculations. It is important to note that these calculations are made by considering the amine donor and anthracene acceptor as separate entities and hence are only approximations.

The change in free energy value for the electron transfer from the tertiary amine moiety to the singlet excited state of the anthracene chromophore is found to be <0 for **1a-h**, which predicts a facile quenching of the anthracene fluorescence by the tertiary amine moiety in **1a-h** through an intramolecular electron transfer mechanism (Table 2). The values are in agreement with the quenching characteristic shown by these compounds. ΔG_{ET} is highest among the series for **1h** (-0.08 eV), which shows the lowest quenching characteristics. Similarly, for **1e, f** and **g**, ΔG_{ET} is low (-0.64, -0.69, -0.66 eV respectively) which shows high quenching in the series.

Table 2. Calculated free energy ΔG_{ET} for anthracene/amine electron transfer; $E_{A/A^-} = -1.97$ eV (Vs. SCE); $E_{0/0} = 3.21$ eV; E_{D/D^+} are taken from literature[67,68]

Compound	$E_{D/D+}$	ΔG_{ET} (eV)	ΔG_{ET} (kcal mol^{-1})
1a	0.80	-0.44	-10.09
1b	0.81	-0.43	-9.87
1c	0.83	-0.41	-9.42
1d	0.89	-0.35	-8.04
1e	0.60	-0.64	-14.71
1f	0.55	-0.69	-15.86
1g	0.58	-0.66	-15.17
1h	1.16	-0.08	-1.83

Compound **1g** showed high efficiency (98%) in PET quenching. The exact reason for the exceptional behaviour of **1g** with respect to its relatives in the series **1a-h** is so far unknown to us. We expect the influential interaction of the oxygen atom in the excited state of the molecule. The highest fluorescence quenching efficiency shown by **1f** (99%) among the series is expected to be due to the presence of a benzyl group on the nitrogen. Presence of an additional arene unit in the molecule increase the possibilities of excited state interactions like intramolecular arene-arene and amine-arene along with usual anthracene-amine interaction. This increases the magnitude of PET there by resulting in more effective quenching. The decay kinetics of **1f** shows multi-exponential type decay that indicates the presence of more than two transient species during the excitation.

Emission spectrum of **2** clearly reveals a vibronically resolved emission band and no board emission. Similarly compounds **1a-h,** also have a

vibronically resolved emission band but there was no exciplex emission observed in the fluorescence emission spectra in solvents like methanol and acetonitrile. The absence of exciplex emission indicates that these solvents are inefficient to stabilise the possible exciplex species in **1a-h** and electron transfer may be taking place directly to form a radical cation-radical anion pair consequently resulting in quenching of locally excited state of anthracene in these molecules. There are reports of exciplex emission in the analogous *N,N*-dimethyl(phenanthren-9-yl)methylamines[69] in highly polar solvent mixtures like DMSO/DMF and H_2O. The decay kinetics of **1a-h** was studied using time-correlated single photon counting technique (TCSPC) in methanol at room temperature. Compounds **1a-h** exhibited biexponential decay, whereas uniexponential decay was observed in the case of **2** (Table 3). There was an enhancement of anthracene fluorescence lifetime τ_2 in **1a-h** compared to **2**. The lifetime τ_1 of **1a-h** are smaller than τ_2 as expected indicating that τ_1 corresponds to short-lived transient species formed in the excited state.

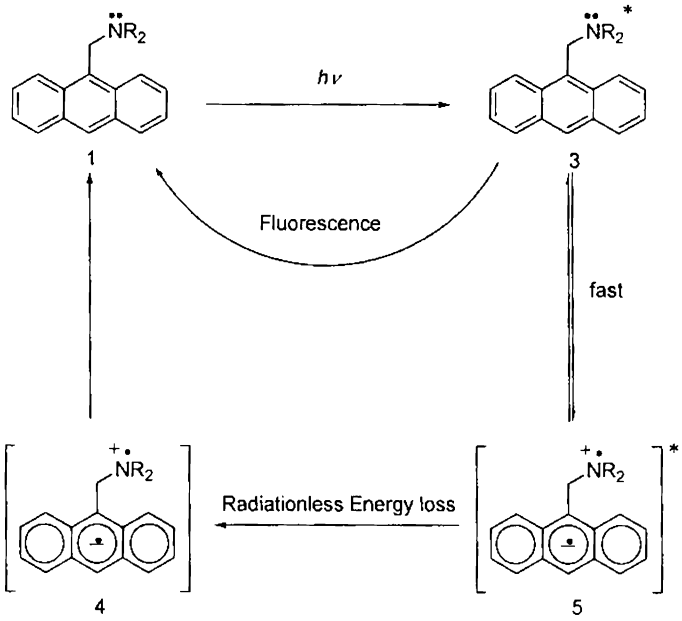
In the photoexcited state, we anticipate that electron transfer takes place from the amine component to anthracene giving rise to a short-lived intramolecular charge transfer (CT) complex **5**. Radiationless energy decay will give rise to a radical cation-radical anion pair **4** followed by charge recombination to generate the parent (anthracen-9-yl)methylamine in the excited state (Scheme 2). The emission from the CT complex **5** has not been detected in the emission spectrum of **1a-h** in methanol or acetonitrile. We propose that **5** is the transient short-lived species (with lifetime τ_1) and remains undetected by the spectrometer.

Table 3. Excited state lifetime of **1a-h**; τ_2 is the local anthracene fluorescence lifetime and τ_1 is the life time of a transient species.

Compound	τ_2 ns	%Composition	τ_1 ns	%Composition
1a	7.83 ± 0.02	96.16	0.87 ± 0.09	3.84
1b	7.89 ± 0.01	95.57	1.61 ± 0.06	4.43
1c	8.16 ± 0.02	96.52	2.31 ± 0.21	3.48
1d	7.43 ± 0.01	97.82	0.52 ± 0.00	2.18
1e	6.37 ± 0.01	86.94	1.64 ± 0.03	13.06
1f	8.80 ± 0.04	*	*	*
1g	6.69 ± 0.01	86.65	0.92 ± 0.25	13.35
1h	5.92 ± 0.01	99.93	2.80 0.74	0.07
2	4.07 ± 0.00	100	-	-

*multiexponential decay

Lifetime of the locally excited state of anthracene chromophore (τ_2) has shown an enhancement in **1a-h**. The decay kinetics shows that the major component present in the excited state is the longer lifetime species corresponding to the local emission from anthracene. The steady state fluorescence emission spectrum shows efficient quenching of anthracene fluorescence by the amine component. This makes clear that the decay of short-lived exciplex/charge transfer species takes place *via* back electron transfer giving rise to the local excited state of anthracene (**3**). Apparently, the minor emitting component with shorter lifetime which is detected only in the TCSPC is expected to be a transient species **5** formed through charge transfer and is expected to be in rapid equilibrium with **3**.



Scheme 2

Hence, the locally excited state of anthracene is populated during the process and the enhancement of lifetime is understood as due to the time delay in electron transfer-back electron transfer process. The highest τ_2 (8.8 ns) in the series is for **1f**, which is understandable as due to the number of excited state processes taking place which are in equilibrium with the local excited state of the molecule *via* reverse electron/charge transfer.

The enhancement in lifetime of anthracene fluorescence can also be due to intersystem crossing to form the triplet excited state of the species. The anthracene triplets formed may again undergo a nonemissive electron transfer process or an intersystem crossing to form singlet excited state. However, there is no evidence so far for the plausible occurrence of a triplet pathway in PET quenching of similar systems.

The quantum yields of fluorescence in **1a-h** in methanol solvent were calculated using equation 2,

$$\Phi_f = \frac{OD_a^0 \; I_f \; \eta_f}{OD_a \; I_f^0 \; \eta_0} \; \Phi_f^0 \qquad (2)$$

where, OD_a^0 and OD_a are the absorbance of standard and unknown, respectively. I_f^0 and I_f are the areas of fluorescence peaks of the standard and unknown, respectively. η_0 (1.3749, *n*-hexane) and η_f (1.3284) are the solvent refractive indices of standard and unknown. Φ_f^0 is the fluorescence quantum yields of the standard (0.4, 9-methylanthracene in *n*-hexane). The relative fluorescence quantum yield of **1a-g** is considerably lower in comparison to **2** and that of **1h** (0.38) is the highest among the series (Table 4).

Applying steady-state approximation to fluorescence quenching, rate of quenching k_{et} is determined from the equation (eq. 3)

$$k_{et} = [(\Phi_f^0/\Phi_f)-1] / \tau \qquad (3)$$

where Φ_f^0/Φ_f is the ratio of the fluorescence quantum yield of the reference to that of **1a-h** and τ is the lifetime of 9-methylanthracene (4.065 ns) in methanol. The values obtained are in accord with the ΔG_{ET} values (Table 4). High rate constant for **1e-g** (5.8×10^9, 11.9×10^9, 10.5×10^9 s^{-1}) explains the ease of quenching in the compounds whereas low rate constant in the case of **1h** (0.0113×10^9 s^{-1}) indicates a lower rate of quenching.

Table 4. Φ_f is the relative quantum yield keeping 9-methylanthracene (Φ_f^0 = 0.4, in *n*-hexane) as standard; OD_a = optical density; I_f = integrated emission intensity; k_{ex}= rate constant.

Compound	OD_a (at λ = 365)	I_f	Φ_f	k_{ex} x 10^{-9} s^{-1}	ΔG_{ET} (eV)
1a	0.025	73.3	0.049	1.7362	-0.44
1b	0.019	76.2	0.067	1.2039	-0.43
1c	0.021	88.0	0.071	1.1405	-0.41
1d	0.020	133.7	0.112	0.6234	-0.35
1e	0.053	46.8	0.015	6.3358	-0.64
1f	0.028	12.5	0.007	12.7726	-0.69
1g	0.016	8.1	0.008	11.3056	-0.66
1h	0.026	548.2	0.357	0.0296	-0.08

Thus we have illustrated the PET behaviour of (anthracen-9-yl)methyl-amines **1a-h** with respect to 9-methylanthracene in methanol solvent. The formation and behaviour of exciplex/charge transfer complex are found to be dependent on several factors. However, an exciplex emission is not observed in these cases when methanol was used as solvent. Ease of PET quenching is dependent upon the redox potentials of the donor and acceptor in these systems. Geometrical requirements for efficient fluorescence quenching through PET with respect to the cyclic amines indicate that as the ring size increase the PET quenching decrease.

3.4. Experimental

3.4.1. General Procedures. Absorption spectra were recorded using Shimadzu 160A spectrometer and Fluorescence emission and excitation spectra were recorded using Varian Cary Eclipse fluorescence spectrometer.

3.4.2. Starting Materials. Solvents were purchased from S. D. Fine Chem. Ltd. and were purified by distillation as per required.

3.4.3. Fluorescence Lifetime Measurements.

Fluorescence decay measurements of the (anthracen-9-yl)methylamines **1a-h** and 9-methylanthracene were carried out using the time correlated single photon counting technique (TCSPC) with micro channel plate photomultiplier tube (MCP-PMT) as detector and picosecond laser as excitation source.

3.4.3.1. Time Correlated Single Photon Counting (TCSPC) Technique.

Fluorescence lifetimes of the fluorophores were measured using various methods. Among all, TCSPC is the best technique due to several advantages. TCSPC is a digital technique, counts the photons that are time correlated with the excitation pulse. The heart of the method is a time to amplitude converter. The sample is repeatedly excited using a pulsed light source. Each pulse was optically monitored by a high-speed photodiode, to produce a start signal, which is used to trigger the voltage ramp of the TAC. The voltage ramp is stopped when the first fluorescence photon from the sample is detected. The TAC provides an output pulse whose voltage is proportional to the time between the start and stop signals. A multichannel analyser converts this voltage to time channel using an analog-to–digital converter. The MCA builds up a probability histogram of counts versus channels by summing over many pulses. The counting is continued until 10,000 counts were collected in the peak channel.

Schematic representation of fluorescence lifetime spectrometer (Model 5000U, IBH, UK) is shown in Fig. 3.1. The second harmonic (375 nm) output from the Tsunami mode locked picosecond laser was used as the exciting source. The mode locked 375 nm laser was focussed in the sample and the fluorescence photons from the sample were collected at right angle to the excitation beam. The emitted photons were detected by a MCP-PMT (Hamamatsu R3809U) after passing through the monochromator (f/3). The photon signal from the MCP-PMT was fed into the CFD and the NIM out from the CFD serves as stop signal in the TAC. The MCP output was directly read on a rate meter.

The start signal for TAC is derived from the high-speed red sensitive silicon photo detector (Thor Labs Inc., DET 210). The fundamental output (750 nm) from the Tsunami mode locked picosecond laser was focussed on the photodiode. The photodiode signal is converted to TTL signal by pulse converter' (IBH, Model TB-01). The output TTL signal from the pulse converter is used as start pulse of the TAC. In our case, the laser source is operated at 4 MHz. The signal from the photodiode is used as stop signal and the signal from the MCP-PMT (Hamamatsu, R3809U) is used as start signal in order to avoid the dead time of the TAC.

The difference between the start and stop signal taken by the pulses travel through the cables and electronics and for the excited state to relax and emit a photon. The TAC output is fed in the MCA Card (Oxford Corporation U.K) and data collection was carried out by the software (Data station 2000) provided by IBH. Repetitive laser pulsing and emitted photon collection produces a histogram of voltage (time) against counts. This histogram represents the measured fluorescence decay. For recording the lamp profile, a scatterer was placed instead of the sample and the same procedure was

reported. The response time of this instrument is around 50 ps.

3.4.3.2. Picosecond Laser Instrumental Description

The diode laser pumped Millenna V (Spectra Physics) CW Nd- YVO_4 laser was used to pump the Ti: Sapphire rod in the Tsunami mode locked picosecond laser (Spectra Physics). The diode laser output was used for the pumping the Nd- YVO_4 rod in the Millenna. It contains two laser diode bars each having 19 diode elements. These diodes have the laser output of 809 nm with the power of 13 Watts, it was taken through the fibre optical bundles to the Millennia.

The diode laser output was focused into the Nd- YVO_4 rod on both sides and produces the output of 1064 nm. This is the fundamental output and is resonated in the "Z" cavity. In this extended "Z" cavity, there is a doubler crystal (Lithium triborate) which is non-critically phase matched and is kept at 144 ^{0}C. The output 532 run is taken through a dichroic output coupler of the Millenna V. The maximum (green, 532 nm) output power from the Millennia was obtained by the Quiet multi axial mode doubling, (QMAD) technology.

The 5W green 532 run laser is used for pumping the mode locked Ti: Sapphire Tsunami laser (Spectra Physics, 3960) which can produce pico/femto pulses by changing the optics. The pump beam incident on the Ti: Sapphire rod at the Brewster's angle. The tuning range of the Ti: Sapphire laser is 690 to 1080 nm. In this investigation the standard optics with the output between 720 and 850 nm was used. The birefringent filters achieve the wavelength selection. The regenerated mode locking of the laser is obtained by Kerr effect. Pulse width of the mode locked Tsunami laser is <2 ps which operates at 82 MHz. The pulse width of the laser is measured using an autocorrelator (Model 409-08, Spectra Physics) which is a device for measuring the duration

of ultrafast pulses. Second harmonic generation with background free configuration technique is used in the autocorrelator. The measured pulse is displayed on a standard high impedance oscilloscope (Scientific, 30 MHz) for real time viewing. The pulse picker (Spectra Physics, 3980) selects the pulse at the rate of 4 MHz from the 82 MHz train of pulses from Tsunami laser.

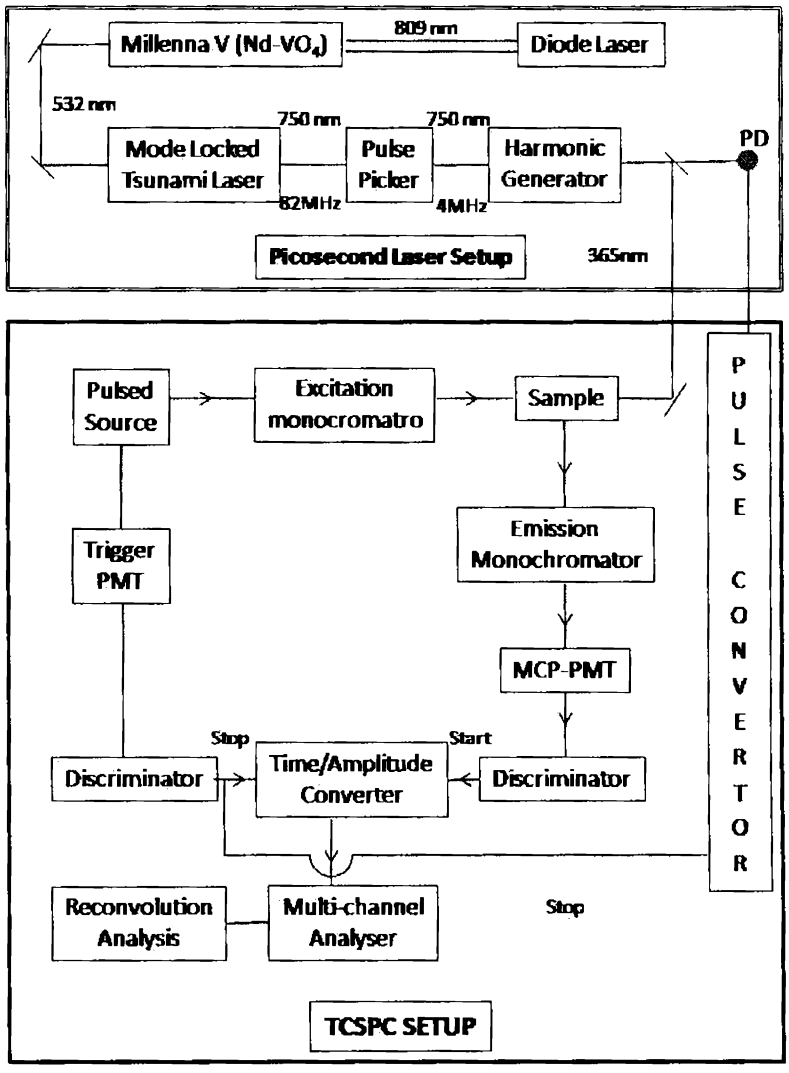


Figure 4. Diagram representing the TCSPC and Picosecond Laser setup

The second and third harmonic laser output is obtained from the flexible harmonic generator (FHG) (Spectra Physics, USA). Second harmonic generation is obtained by focusing the laser from the pulse selector into LBO crystal. For the third harmonic signal both fundamental and second harmonic beams should overlap perfectly in time and space in BBO (Beta Barium Borate) crystal with standard optics Tsunami gives 750 nm as a fundamental output and the second harmonic output from the FHG is 375 nm, which is used for exciting the samples. The emitted photons from the sample are detected at the right angles to the excitation beam, by the high gain Hamamatsu Micro Channel Plate Photomultiplier tube (R 3809U MCP-PMT). The fluorescence photons are collected at the magic angle (54.7°) to avoid the distortions due to the rotational polarisation.

3.4.3.3. Fluorescence Decay Analysis

The measured fluorescence decay is the convolution true fluorescence decay, excitation function and instrument response function. The fluorescence kinetic parameters (lifetime, amplitudes etc.,) are obtained by deconvoluting the excitation and instrument response function from the measured fluorescence decay. The data analysis was carried out by the software provided by IBH (DAS-6) which is based on reconvolution technique using iterative nonlinear least square methods. The reconvolution is preceded by the series of iterations until a χ^2 is reduced to fit 1 ± 0.1. The quality of fit is normally identified by the reduced χ^2, weighted residual and the autocorrelation function of the residuals.

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Chapter - 4

REACTIONS OF (ANTHRACEN-9-YL)METHYLAMINES WITH REACTIVE ACETYLENES

4.1. Abstract

Herein, we discuss the reactions of (anthracen-9-yl)methylamines with different acetylenes. Depending on the solvent used, these amines give a multitude of interesting reactions including electron transfer reactions, nucleophilic substitutions mediated by electron transfer, Michael-type additions and Diels-Alder reactions with suitable acetylenes. We have postulated plausible mechanisms to account for various reactions observed by us.

4.2. Introduction

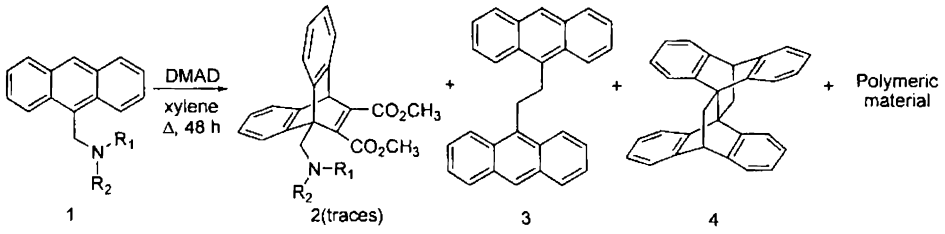
The original purpose of our investigation was to introduce a tertiary amino group at the bridgehead position of dibenzobarrelene to assess the impact of a good electron donor like tertiary amine on triplet-mediated di-π-methane and/or tri-π-methane rearrangement and singlet-mediated cyclooctatetraene formation exhibited by dibenzobarrlene systems.[1] Tertiary amines are well known for their single electron transfer reactions. Consequently, they are efficient quenchers of singlet-excited states of molecules in photochemical reactions. Our idea was to synthesise dibenzobarrelenes with "in built" singlet quenchers. This is anchored on the premise that intramolecular quenching is more efficient than intermolecular

quenching. Based on this, we were interested in examining the photochemistry of amine-appended barrelenes.[2-6] We anticipated to gain access to these dibenzobarrelenes through Diels-Alder reaction[7-10] of corresponding (anthracen-9-yl)methylamines with suitable acetylene dienophiles.

Contrary to our expectations, attempted Diels-Alder reaction between (anthracen-9-yl)methanamines and acetylenes did not yield the expected barrelene derivatives in viable yields. Different unexpected products were formed in these reactions. Depending on the nature of the solvent and acetylene employed, dramatic solvent dependence was observed in these reactions. We present here an overview of these interesting reactions and a detailed analysis of the results obtained in these reactions.

4.3. Results and Discussion

In an attempt to synthesise amine appended dibenzobarrelenes, we carried out the Diels-Alder reaction between the corresponding (anthracen-9-yl)methylamines and a reactive acetylene, such as dimethyl acetylenedicarboxylate (DMAD) in dry xylene under reflux. The choice of solvent here was on the premise that xylene has a boiling point (135 ^{0}C) high enough for successful Diels-Alder reaction in our case. Moreover it would be an ideal solvent for the reaction that proceeds through a relatively nonpolar transition state. In the reaction, we encountered unexpected products such as 1,2-dianthracenylethane (**3**) and lepidopterene (**4**) which indicated electron transfer (ET) and radical reactions in direct competition with conventional Diels-Alder reaction (Scheme 1). The desired amine-appended dibenzobarrelenes were formed only in trace amounts accompanied by extensive polymerisation of DMAD.



Scheme 1

Since the expected Diels-Alder adducts were generated only in trace amounts, we tried to carry out the reaction in other solvents. In polar solvents, Michael type addition of the amine component to DMAD followed by C-N bond cleavage was the predominant reaction. Our attempts to suppress electron transfer and nucleophilic addition pathway by carrying out the Diels-Alder reaction in acidic medium or with protonated amines/ammonium complex with suitable Lewis acids did not afford the required products. The observations are discussed below:

4.3.1. Reactions in Nonpolar Media

When 9-(*N,N*-dimethylaminomethyl)anthracene[11] (**1a**) was refluxed in dry xylene with excess DMAD (1.75 eqv.) under conditions favourable for Diels-Alder reaction, formation of Diels-Alder adduct was not observed in viable yields. The reaction proceeded with high degree of DMAD polymerisation. The expected dibenzobarrelene adduct was formed in trace amounts detectable by GC-MS analysis of the reaction mixture. The reaction yielded two products one of which was fluorescent. Both the products obtained were colourless, nonpolar, crystalline solids with low solubility in common organic solvents and high melting point (mp >310) and were obtained in small amounts. MS data revealed that the two products are isomeric in nature. CHN analysis revealed that the two isomers are simple hydrocarbons sharing the molecular formula $C_{30}H_{22}$. ^{1}HNMR spectrum of the

nonfluorescent compound was conspicuously simple (Figure 1). The peaks at δ 6.71-7.34 showed the presence of a 9,10-ethanoanthracene component. The triplet (δ 4.63, J = 2.5 Hz) and the doublet (δ 2.90, J = 3.0 Hz) with coupling constants less than 3 Hz indicated the presence of a rigid system. Absorption spectrum of this compound revealed the absence of anthracene components and its IR spectrum was indicative of a hydrocarbon structure. Based on these data we identified this compound as lepidopterene[12-17] or tetrabenzotetracyclotetradecatetraene (**4**).

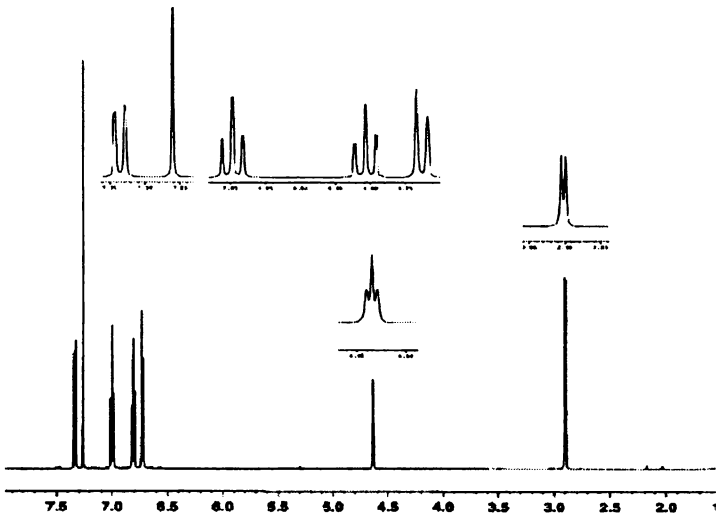


Figure 1. ^{1}HNMR of lepidopterene (**4**)

Structure of **4** was further confirmed by single crystal X-ray analysis that revealed the beautiful butterfly-like geometry for this molecule. The name lepidopterene is coined on the basis of its structural resemblance with species belonging to the lepidoptera family including butterflies, moths and skippers. The ORTEP diagram of **4** indicating its butterfly-like geometry is presented in Figure 2. It may be mentioned here that **4** is generated as one of the products

in several ground and excited state single-electron transfer mediated reactions involving suitably substituted anthracenes.[12-17]

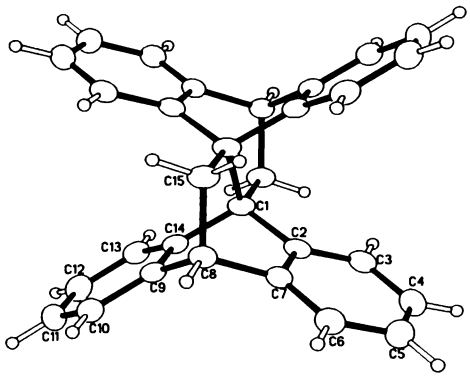
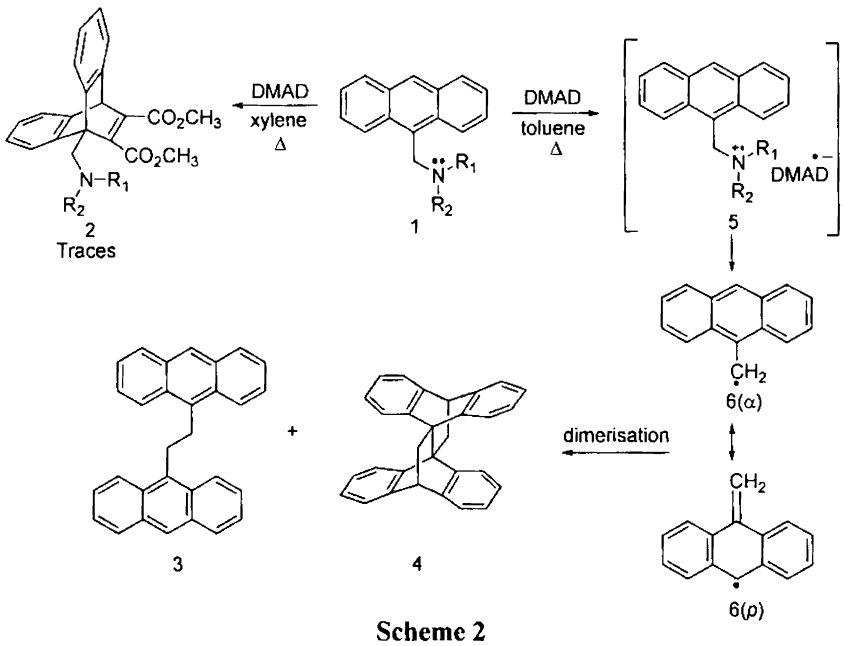


Figure 2. ORTEP diagram of lepidopterene (**4**) obtained through single crystal analysis

The ^{1}H NMR spectrum of the second compound obtained in trace amounts, showed a singlet at δ 4.07 and a multiplet around δ 7.45-8.42 corresponding to a 9-anthracenemethyl component. This compound was identified as 1,2-bis(9-anthracenyl)ethane[16] (**3**) based on ^{1}H NMR and MS data.

Since both **3** and **4** are isomeric in nature and they were generated in the same reaction, we postulated identical genesis for these two compounds. Based on this concept, we short listed possible common intermediates for the generation of **3** and **4**. Concurrent generation of **3** and **4** in these reactions allude to the dimerisation of 9-anthracenemethyl component which in turn is a cue to a radical pathway in the reaction. These results suggest a C-N bond cleavage resulting in the formation of 9-anthracenemethyl radical occurring somewhere along the reaction pathway. In order to ascertain the role of DMAD in the proceedings, we carried out a control experiment by refluxing a concentrated solution of **1a** in xylene under inert atmosphere. Under these

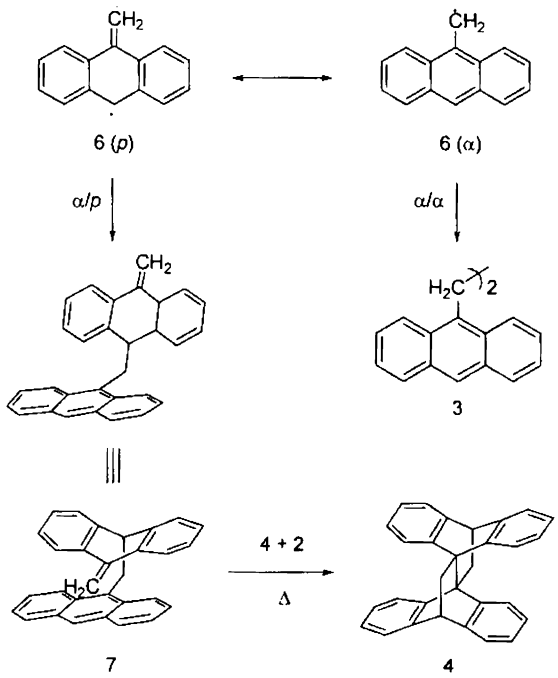
conditions, unchanged **1a** was recovered in near-quantitative amounts even after prolonged refluxing. This result clearly indicated a mechanism entailing a definite role for DMAD. The observed reaction may be viewed to take place through a single electron-transfer from the tertiary amine to DMAD giving rise to radical anion-radical cation pair **5** with concomitant weakening of the C-N bond, followed by a C-N bond homolysis generating the 9-anthracenemethyl radical that may be viewed as a hybrid of **6α** and **6*p*** forms (Scheme 2).



Scheme 2

9-Anthracenemethyl radical thus formed can undergo various reactions depending on the reaction conditions employed. Mostly, in non-polar solvents, it undergoes dimerisation to **3** and **4**.[16] Formation of bisanthracene **3** is visualised in terms of a simple α/α dimerisation. Formation of **4**, on the other hand, involved the *α/p* dimer **7** followed by intramolecular Diels-Alder reaction[13] (Scheme 3). Since 9-methyanthracene was not detected in the

reaction mixture, we conclude that *H*-abstraction by **6** is not competitive with dimerisation.

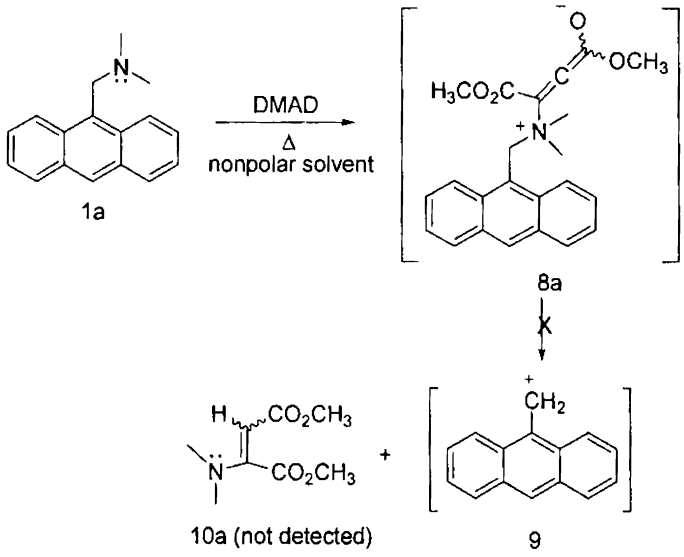


Scheme 3

The preferential formation of dimer **7** over **3** may be explained on the basis of theoretical calculations. AMI calculations[19] have shown that the ground state of the radical **6** has 3-fold higher spin density in the *p* than in the α position, which facilitates the α/p attack to form **7**. As indicated earlier, structure of lepidopterene was established on the basis of spectral data, crystal studies[20] and literature precedence[12-18] (Figure 2). The absence of 9-methylanthracene is not surprising since benzylic radicals prefer dimerisation to hydrogen abstraction from the solvent.[21]

It may be noted that radical formation through single electron transfer and consequent reactions in the anthracenemethanamines-DMAD system occurs in competition with other reactions including: 1) Diels-Alder reaction

between anthracene and DMAD, 2) nucleophilic addition of **1a** to DMAD followed by C-N bond cleavage leading to 9-anthracenemethyl cation and the corresponding *N,N*-dialkylaminofumarate/maleate (**10a**) (Scheme 4).



Scheme 4

In order to gain information on other products formed and to explore the fate of the nitrogen-containing fragment formed in the C-N bond homolysis of **5**, we carried out careful GC-MS and ^{1}H NMR spectral analysis of the crude product mixture obtained from reaction between **1a** and DMAD. GC-MS analysis of the crude reaction mixture indicated the presence of unchanged **1a** in substantial amounts along with a very minor component (*m/z* = 377), attributable to the expected Diels Alder adduct **2a**. Our attempts to isolate this component in pure form were unsuccessful. ^{1}H NMR analysis of the product mixture indicated the presence of **3**, **4** and unchanged **1a** in roughly 1:10:60 ratio. Neither GC-MS nor ^{1}H NMR spectral data indicated the formation of 9-methylanthracene and *N,N*-dimethylaminofumarate/maleate or other possible nitrogen-containing fragments in detectable amounts. Thus, the fate of the

nitrogen-containing fragment is still elusive and there was no indication for the formation of simple *H*-abstraction products of **5** such as 9-methylanthracene.

In order to ascertain the generality of the reaction, we examined the reaction of several (anthracen-9-yl)methylamines **1b-h** (Chart 1) with DMAD in refluxing xylene. We have carefully modulated the electronic and steric environment around the significant nitrogen in these molecules. In all the cases, we observed results analogous with those obtained in the reaction between **1a** and DMAD. Thus, the electron-transfer mediated pathways involving intermediates such as **5** and **6** (*vide supra*) appear to be quite general with several (anthracen-9-yl)methylamines. The amine component formed through the C-N bond cleavage of **5** and/or products formed thereof may be low volatile primary/secondary amines, carbonyl compounds or even ammonia, which are likely to be lost during the course of the reaction or workup of the product mixture. We could not detect any such products from the GC-MS analysis of the reaction mixture either.

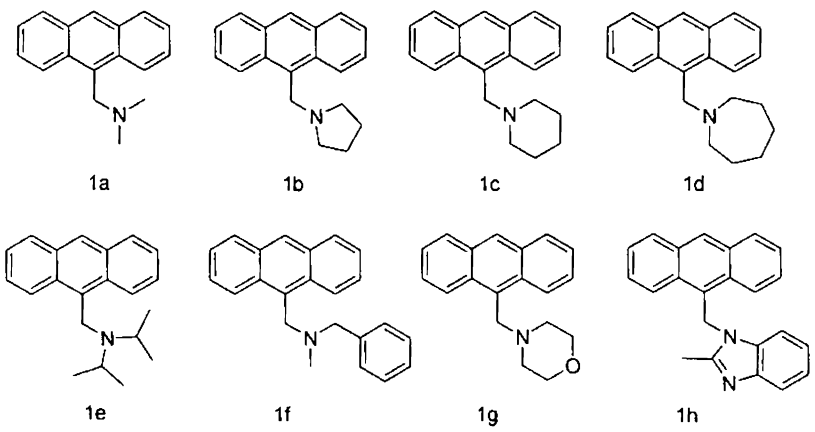


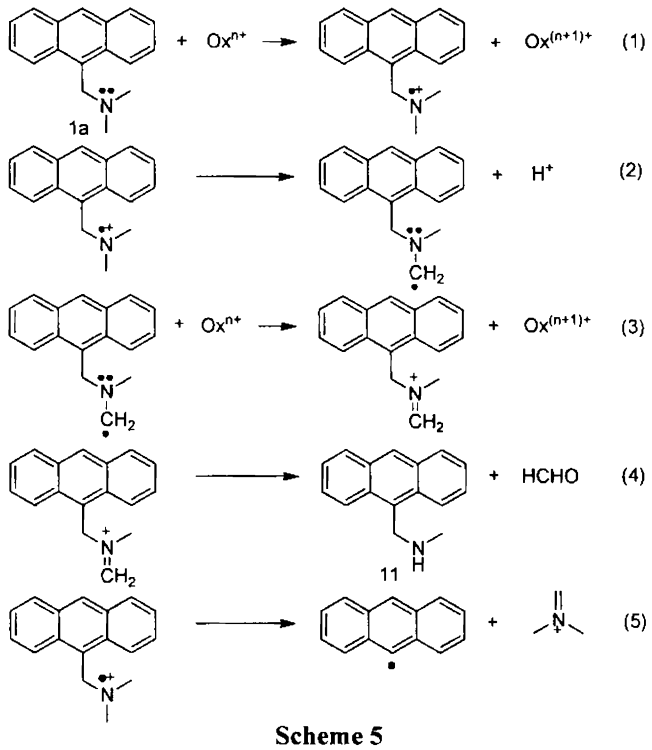
Chart 1

It is interesting to note that even in the case of higher amines **11e,f,h** the amine component formed through the C-N bond cleavage in the reaction was not detected through GC-MS analysis of the reaction mixture. No such products were isolated from these reactions through column chromatography. This led us to the conclusion that a two or three step ET reaction resulting in extensive disintegration may be taking place on the amine components. Complex reaction sequences leading to eventual oxidation to ammonia or a β-proton loss resulting in the formation of an imine appear plausible for the nitrogen-containing fragment. This perception is based on the inference that upon completion of the reaction, the reaction mixture had a perceptible ammoniacal odour. Such reactions have literature precedence.[41-47]

Our observation in these reactions is interesting due to its unorthodox nature. Most of the reported ET reactions of amines take place by an initial one-electron-transfer to an electron sink leading to the formation of a radical ion pair analogous to **5**.[39] A typical electron-transfer mediated fragmentation sequence for tertiary amines is presented in Scheme 5. The radical cation of amine undergoes a β-proton loss giving rise to a carbon radical centered at the β-position (Step 2). Preferential loss of methyl proton indicated herein is dictated by steroelectronic control discussed in Chapter 1. The carbon-centered radical, through a second electron transfer step, further gets oxidised to iminum cation (Step 3), which hydrolyses to the dealkylated amine and a carbonyl compound (Step 4).

Alternatively, β-cleavage resulting alkyl or aryl radical loss (Step 5) is also a distinct possibility. It is also reported that in the oxidation of benzylamines, apart from formation of the dealkylated amine and benzaldehyde, formation of imines, benzonitrile, diazines, anilines, *N*-benzylamines etc have also been observed.[48-53] In many of these reactions,

hydrogen atom abstraction to yield the aminoalkyl radical directly is also feasible depending upon the electron acceptor.[54-56]



Scheme 5

On the contrary, we have observed that DMAD reacts with the (anthracen-9-yl)methylamines in nonpolar solvents following ET as the major pathway which is followed by bond dissociations to give stable 9-anthracenemethyl radical (Scheme 2). The reason for the α-cleavage in the 9-anthracenemethyl side in preference to the other α-methyl groups may be due to the higher stability of 9-anthracenemethyl radical through delocalisation. The *p*-form 9-anthracenemethyl radical is in resonance equilibrium with its *α*-form. This is evident from the fact that formation of lepidopterene takes place *via α/p* coupling. Products arising through β-cleavage such as **11** and those derived from 9-anthracenyl radical were not formed in these reactions.

All the reactions discussed so far are equilibrium reactions and hence increasing magnitude of electron deficiency of the acetylene will enhance ET reaction at the expense of a possible cycloaddition pathway. The observations in these reactions support a radical mechanism for the formation of lepidopterene initiated by a single electron transfer between tertiary amines and the electron deficient dienophiles. Similar radical cations have been invoked as possible intermediates in certain nucleophilic substitution reactions.[23]

Based on these results, we conclude that electron-transfer mediated C-N bond cleavage followed by dimerisation and intramolecular Diels-Alder reaction to form lepidopterene is the major reaction in nonpolar medium employed by us. However, in presence of excess DMAD the expected Diels-Alder adduct was formed in small amounts. The absence of *N,N*-dimethylaminofumarate/maleate in the product mixture rules out the possibility of an ionic mechanism leading to 9-anthracenemethyl cation as depicted in Scheme 4. As expected, at higher temperatures a major portion of DMAD underwent polymerisation.[22]

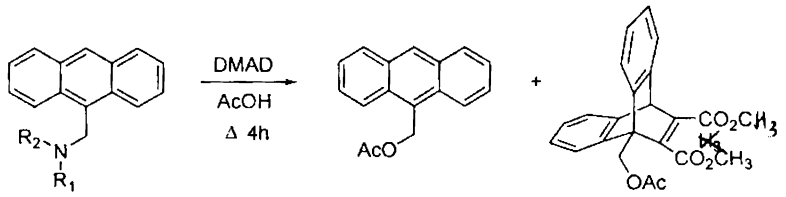
Thus under nonpolar conditions, a novel electron transfer mediated reaction of tertiary amines with highly electron deficient dienophiles such as DMAD leading to the formation of a compound of high structural and synthetic importance: Lepidopterene. Furthermore, our findings are consistent with Pross's intrepretation[24] that the energetics of single electron shift and/or electron transfer dictates the course of organic reactions.

In the reaction, the electron deficient dienophile accepts an electron from the lone pair on nitrogen in preference to cycloaddition with an opulent diene like anthracene. We anticipated that if the lone pair on the nitrogen is protected, electron transfer between amine and acetylene components can be

reduced there by facilitating Diels-Alder reaction. Thus we decided to carry out the reaction with (anthracen-9-yl)methylamines where the lone pair on nitrogen is protected either through protonation or salt formation. When we carried out reactions aimed at cashing on this possibility, we encountered perplexing results which are discussed below.

4.3.2. Reactions in Polar Protic Media - Carboxylic Acids

In an attempt to minimise the electron transfer reaction and thereby to increase the yield of the Diels-Alder adduct **2**, we repeated the reaction of **1a** with DMAD in glacial acetic acid under reflux for 2 hours. The results were surprising. We obtained (anthracen-9-yl)methyl acetate[25] (**12**) and the corresponding barrelene **13**[26] derived thereof, from the reaction mixture along with some amount of unchanged **1a** (Scheme 6). Formation of **12** under these conditions is envisaged as arising through a substitution reaction/solvolysis initiated by electron transfer (Scheme 7).



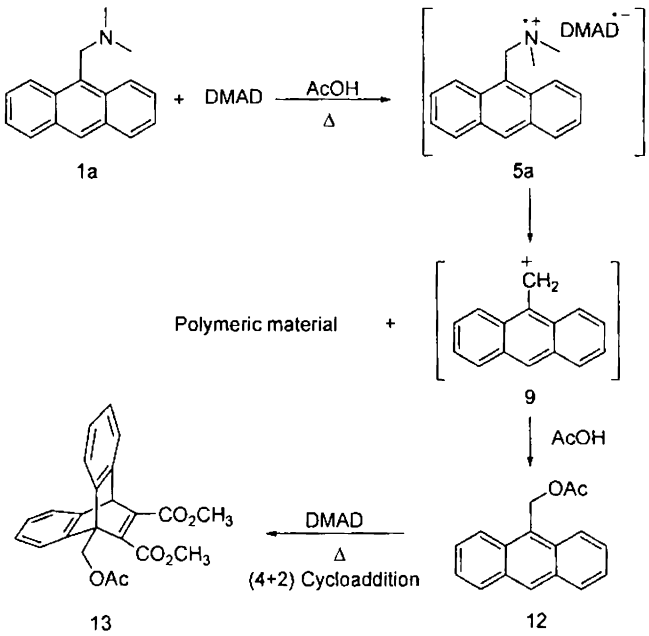
1a 12 13

Scheme 6

We propose that the reaction takes place through the initial transfer of an electron from the amine lone pair to DMAD leading to the weakening and eventual cleavage of C-N bond. Similar C-N bond cleavage, in presence of excess of electron withdrawing acetylenes[27-31] and other oxidising agents[32] has literature precedence. However, the exact nature of C-N bond cleavage is debatable. We propose SN1 type mechanism involving heterolytic cleavage of C-N bond leading to 9-anthracenemethyl cation based on the following

premises: 1) protic solvents such as acetic acid stabilise cations, 2) acetic acid is a poor nucleophile, hence S_N2 type mechanism involving **5a** is not favoured and 3) no product derived of 9-anthracenemethyl radical such as lepidopterene and 1,2-dianthracenylethylene could be isolated from the reaction mixture,[33-36] indicating that homolytic C-N bond cleavage leading to 9-anthracenemethyl radical and its subsequent oxidation to 9-anthracene-methyl cation (**9**) is not operating here.

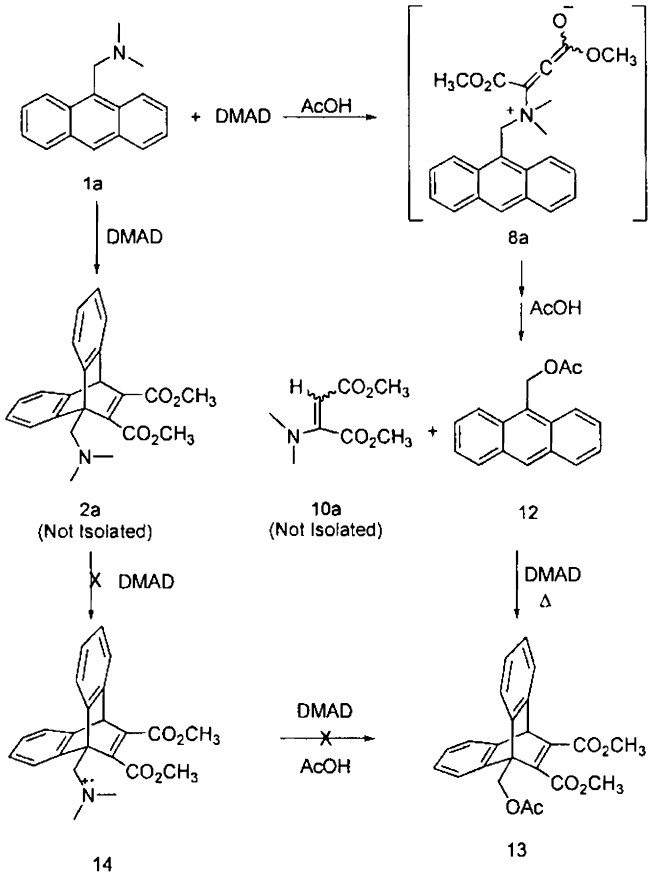
The 9-anthracenemethyl cation formed directly from **5a** is captured by acetic acid to give **12**. Subsequently, **12** undergoes (4+2) cycloaddition with excess DMAD present in the reaction mixture to give the Diels-Alder adduct **13**.[25] In order to assess the role of DMAD on the observed transformations of **1a**, we carried out a blank run by refluxing a solution of **1a** in acetic acid for 2 h. Unchanged **1a** was recovered in near-quantitative amounts from this blank run indicating the involvement of DMAD in the observed solvolysis reaction.



Scheme 7

Alternatively, this reaction could proceed through an ionic mechanism, involving nucleophilic addition of **1a** to DMAD to give **8a**, followed by cleavage of C-N bond leading to the formation of **9** and the corresponding fumarate/maleate **10a** as depicted in Scheme 8.[37] With a view to ascertain this possibility, we carried out GC-MS and NMR analyses of the crude product mixture. We recorded the GCMS analysis of the reaction mixture at times t = 0, 15, 30, 45 and 60 minutes. The results indicated the absence of fumarates/maleates **10a** in the product mixture indicating that they are either not formed or undergo further transformations under the reaction conditions employed by us. To discount the latter possibility, we treated independently synthesised **10a** with excess DMAD in refluxing acetic acid. GC-MS analysis of the product mixture indicated the presence of unchanged **10a** in substantial amounts. These results clearly indicate that if **10a** were formed in the reaction between **1a** and DMAD, at least part of it will survive under the conditions employed by us. While these results discount the alternative possibility of nucleophilic addition followed by bond heterolysis, they further support our claim on ET mediated nucleophilic substitution.

It may be argued that **13** is generated by further transformations of initially formed Diels-Alder adduct **2a** (Scheme 8). However, GC-MS and NMR analyses of the crude reaction mixture did not indicate the presence of **2a** in the product mixture. Based on the absence of **2a** in the product mixture and the low propensity of neopentyl systems like these to undergo nucleophilic substitution reaction through both SN1 and SN2 mechanisms,[23,38] we ruled out a mechanism involving the intermediacy of **2a**. Unreacted DMAD was absent in the product mixture which led us to the conclusion that DMAD underwent amine-initiated polymerisation.[37b] However, since **12** is formed in substantial amounts in these reactions, we conclude that the conditions adapted by us are suitable for Diels-Alder reactions to occur.

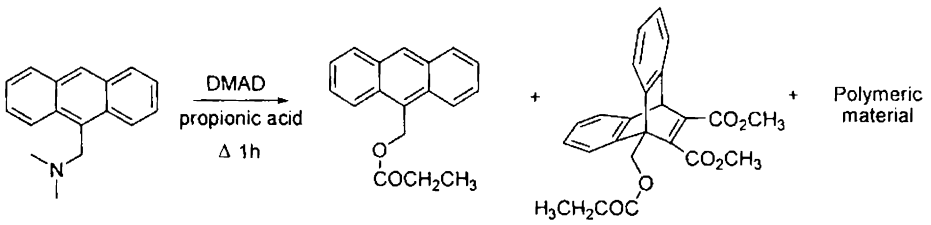


Scheme 8

We carried out the reactions using (anthracen-9-yl)methylamines **1b-h** and observed similar results as with **1a**. As in the case of reactions in nonpolar solvents, the fate of the amine radical formed in this case is uncertain: we surmise that volatile products which escaped detection were formed from these.[39] It is interesting to note that under these conditions (even in the presence of excess of DMAD), in the case of **1a-h**, ET competes with (4+2) addition, leading exclusively to electron transfer mediated nucleophilic substitution followed by (4+2) addition. Again here, the results are consistent with Pross's interpretation that the energetics of single electron shift and/or electron transfer dictates the course of organic reactions.[28] Our observations

on the reaction of **1a-h** in acetic acid represent a rare instance of a highly efficient ET-mediated nucleophilic substitution reaction.

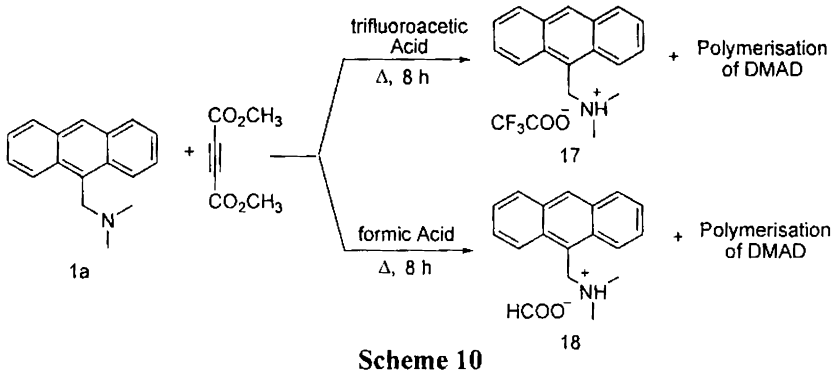
We repeated the reaction between (anthracen-9-yl)methylamines and DMAD in other acids. When the reaction was carried out in refluxing propionic acid using **1a** and DMAD, (anthracen-9-yl)methyl propionate[40] **15** and the corresponding (4+2) cycloadduct **16** was obtained (Scheme 9). The reaction here was much faster than in acetic acid which is attributed to the increase in reaction temperature.



1a 15 16

Scheme 9

We carried out the reaction of **1a** with DMAD in nonnucleophilic carboxylic acid like trifluoroacetic acid (TFA) and formic acid. Formation of stable salts prevented further reaction in these solvents. Neither electron transfer nor cycloaddition pathways were operating in these cases.



Scheme 10

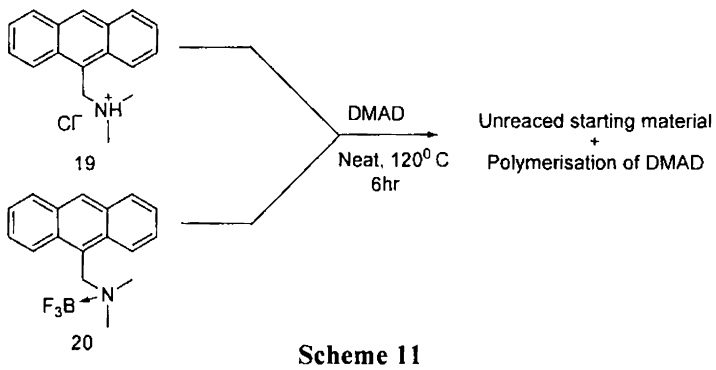
In acetic acid solvent, we have illustrated an electron transfer reaction of (anthracen-9-yl)methylamines with highly electron deficient acetylene like DMAD leading to nucleophilic substitution, under conditions suitable for a thermal (4+2) cycloaddition. This complies with the possibility of nucleophilic substitution through electron transfer in (anthracen-9-yl)methylamines like systems and thus could provide an alternative pathway to accomplish substitution on compounds that are reluctant to undergo classical nucleophilic substitution reactions due to the presence of poor leaving groups. However our attempts to develop viable routes for the synthesis of (anthracen-9-yl)methylamine-DMAD adducts remained unsuccessful under these conditions.

4.3.3. Reactions using Salts of (Anthracen-9-yl)methylamines

We had observed that in the reaction between (anthracen-9-yl)methylamines and DMAD in triflouroacetic acid, the salts of (anthracen-9-yl)methylamines were isolated as stable end products. Based on this observation, we concluded that the salt of **1a** would react with DMAD with diminished propensity for electron transfer and thereby increasing the viability of Diels-Alder reaction. The BF_3 salt of (anthracen-9-yl)methylamine was obtained by treatment of an equimolar mixture BF_3.etherate and **1a** in dichloromethane under stirring for 2 hours at room temperature. The precipitated salt was filtered and washed with dichloromethane to obtain the salt in pure form. To obtain HCl salt of **1a**, gaseous HCl was passed through an ether solution of **1a** under constant stirring. When the solution was saturated with HCl, hydrochloride salt of amine precipitated out, which was filtered out and washed with dry ether to obtain in pure form.

When the reaction was carried out using these salts of (anthracen-9-yl)methylamines, with DMAD under neat conditions, we observed extensive

polymerisation of DMAD. No products corresponding to electron transfer pathways or cycloaddition pathways were isolated from the reaction. Substantial portions of unchanged amine salts were recovered from the reaction mixture.



Scheme 11

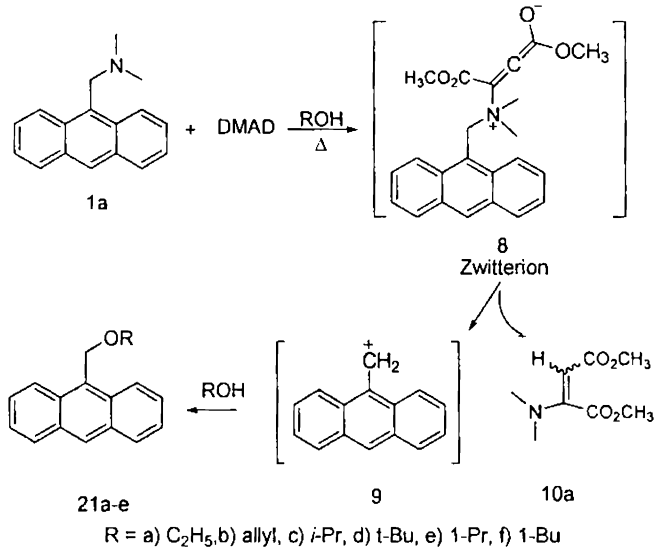
Hence, protection of lone pair through salt formation was successful in eliminating the electron transfer reaction between the amine component and DMAD but was not fruitful in facilitating cycloaddition reaction pathways. At this point we put our goal of synthesising (anthracen-9-yl)methylamine-acetylene cycloadduct on hold and decided to explore the interesting solvent dependent pathways in the reaction of (anthracen-9-yl)methylamines with acetylenes.

The reaction showed varying observations in nonpolar solvents and carboxylic acids. Our next question was what would be the nature of the reaction in other protic solvents like alcohols? The answer was made clear in terms of solvent dependence of these reactions. The results are as discussed below.

4.3.4. Reactions in Polar Protic Media - Alcohols

When **1a** was reacted with excess DMAD in refluxing methanol for 8 hours, 9-(methoxymethyl)anthracene (**21**)[58] and *N,N*-dimethylaminomaleate/

fumarate **10a**[57] were formed and isolated in good yields (78%). We propose that the reaction takes place through the nucleophilic attack of amine on DMAD in a Michael type addition pathway giving rise to a Michael adduct/Zwitterion **8** (Scheme 12). This leads to the weakening and eventual cleavage of C-N bond giving rise to 9-anthracenemethyl cation **9** and aminomaleate/fumarate (**10**).



R = a) C_2H_5,b) allyl, c) *i*-Pr, d) t-Bu, e) 1-Pr, f) 1-Bu

Scheme 12

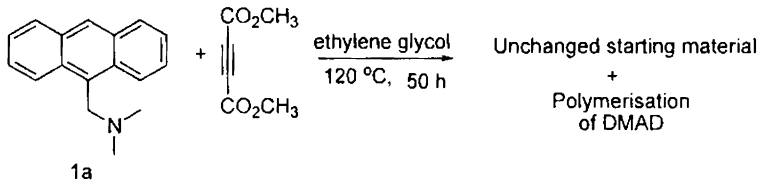
The 9-anthracenemethyl cation formed is captured by the solvent to give the corresponding ether. Alternatively, solvent-assisted SN2 substitution in **8** will also lead to the formation of products such as **21** and **10**. We favour SN1 mechanism in this case based on steric factors and polar protic nature of the solvent employed. In a low-boiling solvent like methanol, Diels-Alder reaction between (anthracen-9-yl)methylamine or 9-(methoxymethyl)anthracene (**21**) and DMAD is unlikely to occur.

In order to generalize the pathways depicted in Scheme 13, we employed several alcohols like ethanol, 1-propanol, 1-butanol, allyl alcohol, 2-propanol,

t-butanol etc. In all cases, respective (anthracen-9-yl)methyl ether was formed in good yields along with aminoalkylmaleate/fumarates.

The rate of the reaction was dependant on boiling point of the alcohols used. The reaction was faster in higher boiling allyl alcohol, 1-propanol, *t*-butanol, 1-propanol and 1-butanol when compared to methanol and ethanol. In the case of 1-propanol and 1-butanol, the GC-MS analysis of the reaction mixture showed that along with the expected products there were impurities corresponding to isomeric products of **21** in the reaction mixture. This may be due to the isomeric alcohol impurities present in the commercial sample of alcohol used by us. However, isolation of ethers in the case of 1-butyl and 1-propylalcohols in pure form was not achieved from the complex reaction mixture.

We employed a diol such as ethylene glycol as solvent in the reaction of **1a** with DMAD under constant stirring at 120 ^{0}C. There was no observable reaction in this case. Only unchanged starting material was recovered even after 50 hours of reaction (Scheme 13).



Scheme 13

This shows that the viscosity of the solvent employed has a definite effect on the reaction rate. The reaction rate for bimolecular reactions is inversely related to viscosity of the solvent. Nucleophilic addition of amine to DMAD being a bimolecular process was hindered by increased viscosity of the solvent. We had earlier observed that Diels-Alder reaction between anthracenes and DMAD (*cf*: formation of **13**) is feasible below 120 ^{0}C. Our

observations indirectly provide information on suppression of Diels-Alder reactions in viscous solvents. In conclusion, the rate of the reaction between (anthracen-9-yl)methylamine and DMAD is influenced by reaction temperature and polarity, viscosity and nucleophilicity of the solvent.

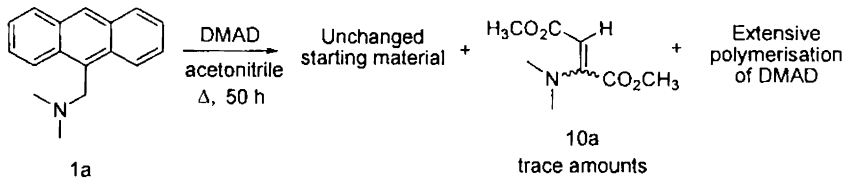
Other (anthracen-9-yl)methylamines **1b-h** reacted in the same fashion with DMAD in alcohol solvents. Compounds **10b-h** were formed in good yields (52-75%). In alcohol solvents the reaction proceeds through a completely ionic pathway giving rise to 9-anthracenemethyl cation and the products derived thereof. Thus we have illustrated a nucleophilic substitution of (anthracen-9-yl)methylamines **1a-h** taking place via Michael type addition of **1a-h** to DMAD.

4.3.5. Reactions in Polar Aprotic Media

We were interested to explore the outcome of the reaction in non-nucleophilic polar solvents or aprotic solvents such as acetonitrile, dioxan etc. We carried out the reaction of **1a** with excess DMAD (2 eqv.) in acetonitrile under refluxing conditions. DMAD underwent extensive polymerisation. GC-MS analysis of the reaction mixture indicated unchanged starting material even after 72 hours of reaction. Trace amounts of dimethylaminomaleate/fumarate **10a** was also identified from the GC-MS analysis of the reaction mixture. There was no evidence of the anthracene counterpart in the GC-MS analysis of the reaction mixture. Though TLC analysis of the reaction mixture indicated the formation of a few fast-moving components in minor amounts, our attempts to isolate them in pure form were unsuccessful.

The reaction showed similar characteristics in other polar aprotic solvents like *N,N*-dimethylformamide, 1,4-dioxan and chlorobenzene.

Extensive polymerisation of DMAD was observed and unchanged starting material was recovered in all cases.



Scheme 14

The lack of reactivity observed in polar aprotic solvents may have two possible explanations. Both ET and ionic pathways may be taking place here. Unlike nonpolar and polar protic solvents, polar aprotic solvents form large solvent cages. It appears that the radical cation-radical anion pair formed by initial single electron transfer and/or the Michael adduct are trapped inside the large solvent cages. Back electron transfer or reversion of Michael adduct within the cage will regenerate the starting materials with consequent loss of chemical reactivity. Due to this, no net reaction is observed or we can assume that an energy wastage process is the overall result in reactions in polar aprotic media. Some of the Michael-type adduct formed may undergo further reactions to give dialkylaminomaleate/fumarate which is found in trace amounts and as it stands of now, the fate of anthracene component is unknown to us. A small portion of the solvent encapsulated radical cation/anion pair may diffuse out of the solvent cavity initiating a high turnover process like DMAD polymerisation.

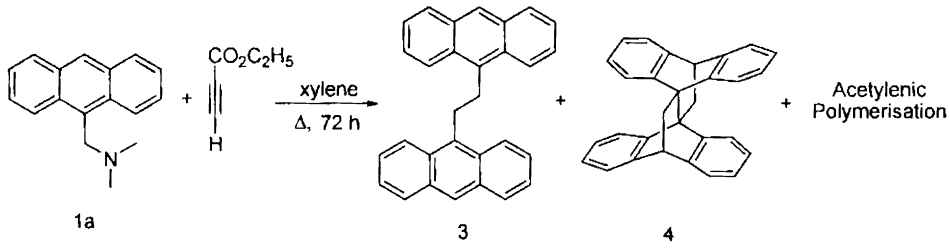
4.3.6. Influence of Acetylene in the Reaction

To study the influence of nature and reactivity of acetylene in the reaction, we employed several acetylenes with differing reactivity in the above reactions such as ethyl propiolate, dibenzoylacetylene, phenylacetylene and diphenylacetylene. Reactivity of acetylene depends upon substituents present.

Electron withdrawing groups increase the electron deficiency of the acetylene thereby increasing the reactivity. We observed dramatic change in reactivity depending on the solvent and the reactivity of acetylenes employed. The results are as follows:

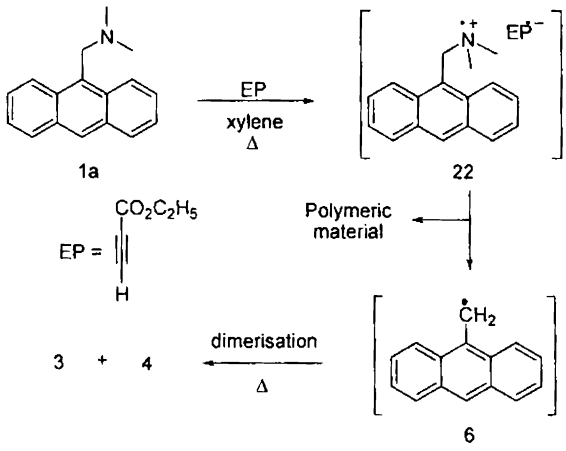
4.3.6.1. Reactions with Electron Deficient Acetylenes Other Than DMAD

We employed acetylenes like ethyl propiolate and dibenzoylacetylene in the reactions and found similar observations as in the case of DMAD. Ethyl propiolate, with only one electron withdrawing substituent is less reactive than DMAD. Reaction of **1a** with ethyl propiolate in nonpolar conditions followed electron transfer pathways giving products **3** and **4** as in the case of DMAD (Scheme 15).



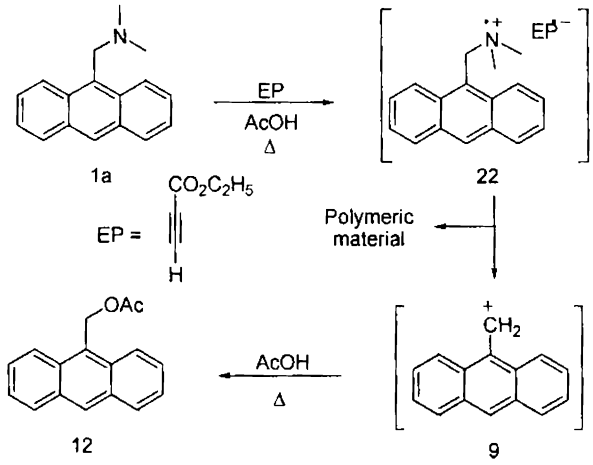
Scheme 15

We did not find the formation of amine-acetylene Diels-Alder adduct similar to **2a** in this case. The rate of the reaction was found to decrease in this case. This is due to the decrease in reactivity of the acetylene in comparison with DMAD. The mechanism operating here is same as that of DMAD, proceeding with a single electron transfer from amine to ethyl propiolate giving rise to a radical cation radical anion pair **22**, which further undergoes homolytic C-N bond cleavage to give 9-anthracenemethyl radical **6**. Radical **6** undergoes dimerisation reactions as explained in Scheme 3.



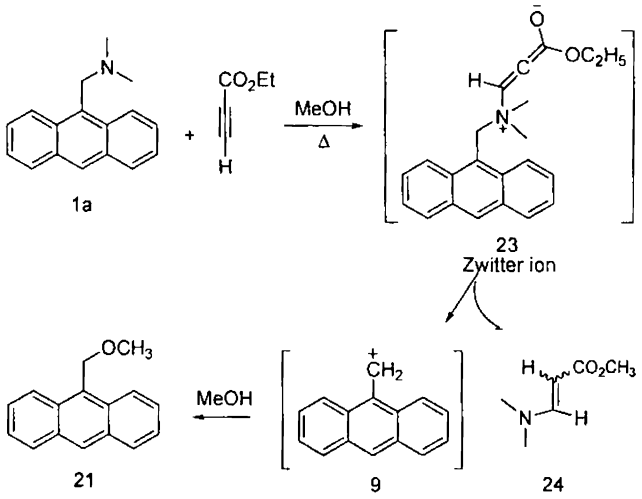
Scheme 16

The reaction in acetic acid using ethyl propiolate also showed the same observations as that with DMAD, with a decrease in the reaction rate (Scheme 17). Again, the formation of Diels-Alder adduct was not found in this case due to lower reactivity of ethyl propiolate towards Diels-Alder reaction under the conditions employed. Hence, in acetic acid solvent, electron transfer mediated nucleophilic substitution reactions is the only observed process in the reaction for ethyl propiolate



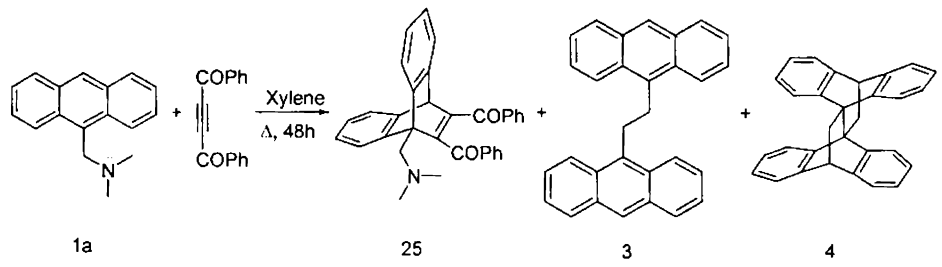
Scheme 17

When we carried out the reaction in methanol solvent using **1a** and ethyl propiolate we found the formation of the 9-(methoxymethyl)anthracene (**21**) along with the (*E/Z*)-3-dimethylaminoethylacrylate[59] (**24**) as in the case of reactions with DMAD. This supports an ionic mechanism taking place in a Michael type fashion through the formation of the zwitterionic intermediate followed by heterolytic C-N bond cleavage to give **21** and **24** (Scheme 18). The rate of the reaction decreased when compared to reaction with DMAD. This is due to the reduced reactivity of ethyl propiolate *vis-à-vis* DMAD.



Scheme 18

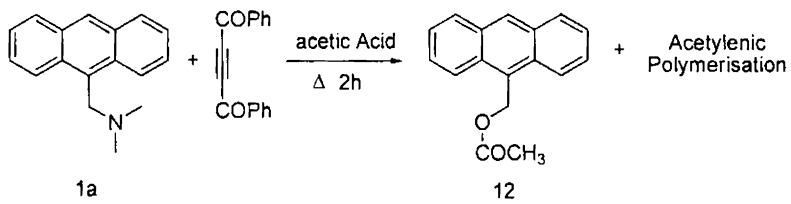
In the case of dibenzoylacetylene (DBA), reaction of **1a** with DBA in refluxing xylene gave the cycloadduct **25** in substantial amounts along with the electron transfer medicated products **3** and **4** in appreciable amounts (Scheme 19). This shows that, in the case of DBA, both the cycloaddition and electron transfer pathways are feasible. Hence, for reaction in nonpolar solvents, the competing electron transfer and cycloaddition reactions depends on the nature of the acetylene. The predominance of these pathways is a function of electron deficiency of acetylene.



Scheme 19

The reaction of DBA with **1a** in acetic acid gave **12** along with a polymeric material with no presence of 2-(dimethylamino)dibenzoylethylene in the reaction mixture (Scheme 20). This indicates the electron transfer mediated nucleophilic substitution pathway similar to that observed with DMAD in the reaction. Absence of the cycloadduct formed form **12** and DBA similar to **13** may be due to the lesser reactivity of DBA towards Diels-Alder reaction at that reaction temperature (118 ^{0}C).

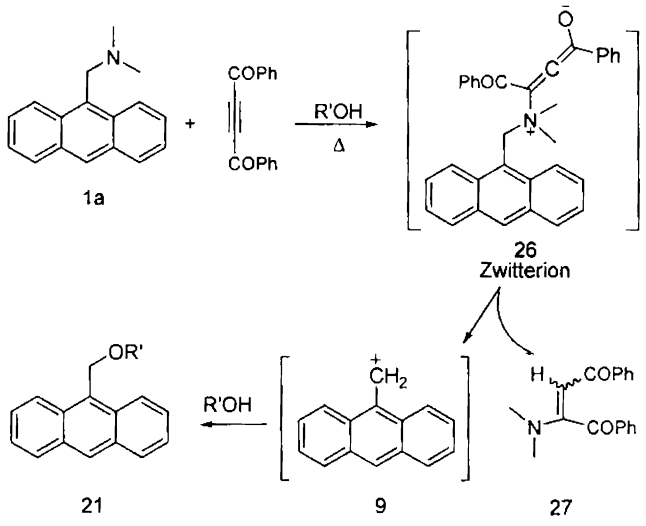
In the mechanism, a single electron transfer from the amine to DBA takes place giving rise to the radical ion pair. The radical ion pair formed will undergo a heterolytic C-N bond cleavage to generate the carbocation **9**, which will be trapped by the solvent to give **12**.



Scheme 20

Similarly, for the reactions in methanol solvent, DBA reacts in the same fashion as in the case of DMAD and ethyl propiolate. Here, a nucleophilic addition of amine to DBA takes place in a Michael type fashion giving the

zwitterion **26**, which undergo a C-N bond heterolysis to 9-anthracenemethyl cation and (*E/Z*)-2-(dimethylamino)dibenzoylethylene[60] (**27**) (Scheme 21).



Scheme 21

Thus, ethyl propiolate and DBA react in similar ways as that with DMAD with slower reactivity in the case of ethyl propiolate. In all the cases, we observed that the nucleophilic substitution takes place competing (4+2) cycloaddition of **1a** and the acetylene. The reactivity of the acetylene used had a direct influence on the mechanism and rate of the reaction in polar as well as nonpolar media.

4.3.6.2. Reactions with Phenylacetylene and Diphenylacetylene

The role of reactivity of acetylene in the reaction can be easily understood by making use of acetylenes like phenylacetylene (PA) and diphenylacetylene (DPA) in the reaction. These acetylenes, having phenyl substituents, are less reactive in comparison with acetylenes having strongly electron-withdrawing substituents. We employed PA and DPA in these reactions and, as expected, the reaction was very slow in all cases. PA and

DPA were found unreactive towards **1a** in non-polar solvents like benzene, toluene and xylene under refluxing conditions even after 72 hours of reaction. We chose a solvent of higher boiling point such as *o*-dichlorobenzene (bp 182 ^{0}C) to increase the reaction temperature. When **1a** was refluxed with DPA in *o*-dichlorobenzene for 96 hours trace amounts of **28** was obtained with recovery of >75% of **1a**. Structure of **28** was arrived at on the basis of spectral and analytical data. The singlet at δ 5.4 in the ^{1}H NMR corresponds to the bridgehead proton in **28** (Figure 3). A small quantity of DPA underwent polymerisation to give hexane soluble oligomers with high degree of visible fluorescence.

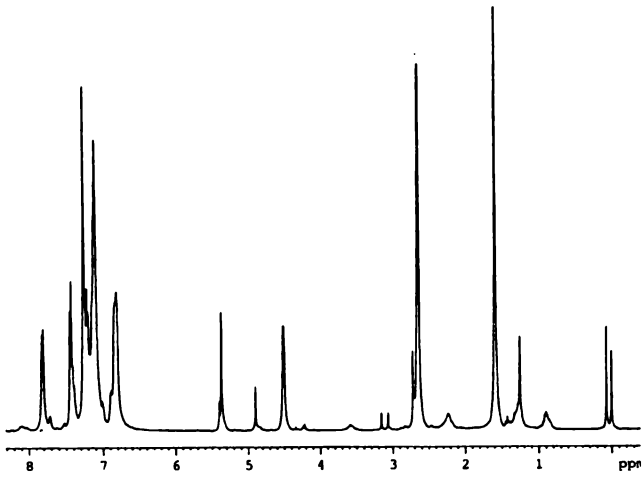
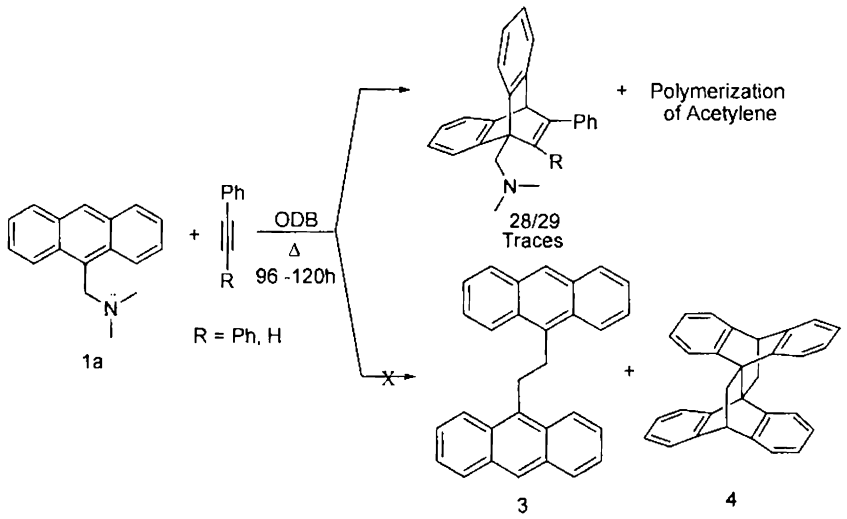


Figure 3. ^{1}H NMR of compound **29**

The observation was similar when phenylacetylene was used in the reaction. Here the reaction was much slower than with diphenylacetylene. Diels-Alder adduct **30** in this case was detected only through the GC-MS analysis of the reaction mixture after the reaction was carried out in *o*-dichlorobenzene for over 120 hours. As expected formation of electron transfer products were undetected from these reactions. They were found

unreactive towards the electron transfer mediated pathways. Their reluctance to undergo electron transfer mediated reactions is due to the fact that PA and DPA are poor electron acceptors when compared to acetylenes like DMAD. The radical ion pairs or Michael type adducts formed by PA or DPA will not be stabilized due to the lack of electron withdrawing groups and thus these pathways will be not favoured.



Scheme 22

This shows that the magnitude of electron deficiency of the acetylene has a definite influence on the mechanistic pathways of the reaction. An increase in the electron deficiency increases the rate of the reaction in both polar and nonpolar solvents and favours electron transfer mediated pathways in non-polar reactions.

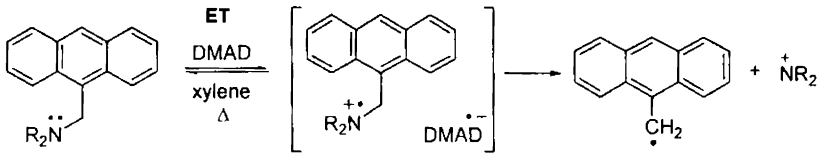
4.4. Conclusion

We have illustrated interesting solvent dependent reactions of a few (anthracen-9-yl)methylamines with reactive acetylenes and explored the mechanistic underpinnings of these reactions under different conditions. (Anthracen-9-yl)methylamines **1a-h** show dramatic changes in the

mechanistic pathways of their reactions with reactive acetylenes depending on the solvent of choice, nature and reactivity of acetylene employed and reaction conditions. Nature of solvent alters the mechanism of the reaction from radical to ionic pathways. Increase in the reaction temperature increases the rate of reaction in general.

(Anthracen-9-yl)methylamines react with acetylenes giving electron transfer pathways and Michael type reactions in competition with the well known Diels-Alder reactions. It is important to note that the reactive acetylenic dienophiles are found to attack the nitrogen lone pair in place of the conventionally electron rich diene like anthracene in the molecule under the conditions favourable for Diels-Alder reaction.

For reactions in nonpolar solvents, a novel electron transfer mediated reaction of tertiary amines with highly electron deficient dienophiles such as DMAD leads to the formation of a compound of high structural and synthetic importance: lepidopterene.

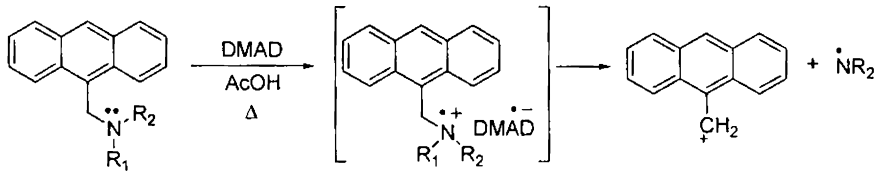


Scheme 23

In summary, we conclude that electron-transfer mediated homolytic C-N bond cleavage followed by dimerisation and intramolecular Diels-Alder reaction to form lepidopterene is the major reaction under non-polar reaction conditions employed by us.

The reactions in carboxylic acids are shown to undergo a one electron transfer reaction of (anthracen-9-yl)methylamines with electron deficient

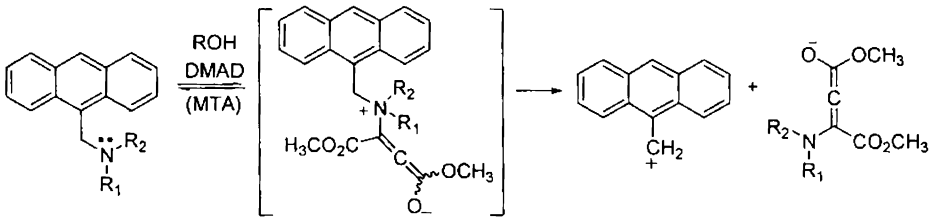
acetylene like DMAD leading to nucleophilic substitution, under conditions suitable for a thermal (4+2) cycloaddition. This in turn alludes to the possibility of electron-transfer mediated substitution reactions in the case of (anthracen-9-yl)methylamines.



Scheme 24

The reaction follows a general mechanism of an initial electron transfer from ~~acetylene~~ amine to ~~amine~~ acetylene followed by heterolytic C-N bond cleavage to give 9-anthracenyl cation and products derived thereof. This complies with the possibility of nucleophilic substitution through electron transfer in (anthracen-9-yl)methylamines like systems and thus could provide an alternative pathway to accomplish substitution on compounds that are reluctant to undergo classical nucleophilic substitution reactions due to the presence of poor leaving groups. Protection of amine lone pair through salt formation helps in minimising the ET mediated pathways but does not favour the cycloaddition pathway in (anthracen-9-yl)methylamines.

(Anthracen-9-yl)methylamines are shown to react with electron deficient acetylene like DMAD in alcohol solvents following a Michael type addition of amine to DMAD to form a zwitterion which further undergo a heterolytic C-N bond cleavage to give 9-anthracenemethyl cation and dialkylaminomaleate /fumarate. The reaction has produced a variety of 9-anthracenemethyl ethers corresponding to the alcohol used. The viscosity of the solvent plays a definite role in deciding the reaction rate.



Scheme 25

In polar aprotic solvents, the acetylene employed undergoes extensive polymerisation and major portion of unchanged starting material was recovered along with trace amounts of dialkylaminomaleate/fumarate. Traces of dialkylaminomaleate/fumarate formed indicate the possibility of an ionic type mechanism predominating in the reaction. The lack of reactivity observed in polar aprotic solvents may be explained in terms of a cage effect. It appears that the radical cation-radical anion pair formed by initial single electron transfer and/or the initial Michael adduct are trapped inside the large solvent cages. Back electron transfer or reversion of Michael adduct within the cage will regenerate the starting materials and consequent net loss of chemical reactivity.

The nature and reactivity of acetylene is shown to have definite role in their reactions with (anthracen-9-yl)methylamines. The magnitude of electron deficiency of the acetylene controls the mechanistic pathways of the reaction. An increase in the electron deficiency increases the rate of the reaction in both polar and nonpolar solvents and favours ET mediated pathways in non-polar reactions. Acetylenes like DBA follows cycloaddition as well as ET mediated pathways in nonpolar media. The less reactive PA and DPA are found unreactive towards ET mediated pathways. They give the expected Diels Alder adduct in trace amounts when reacted with (anthracen-9-yl)methylamines at temperatures above 180 ^{0}C.

4.5. Experimental.

4.5.1. General Procedure

All melting points are uncorrected and were determined on a Neolab melting point apparatus. All reactions and chromatographic separations were monitored by thin layer chromatography (TLC). Glass plates coated with dried and activated silica gel or aluminium sheets coated with silica gel (Merck) were used for thin layer chromatography. Visualisation was achieved by exposure to iodine vapours or UV radiation. Column chromatography was carried out with slurry-packed silica gel (Qualigens, 60-120 mesh). Absorption spectra were recorded using Shimadzu 160A spectrometer and infrared spectra were recorded using ABB Bomem (MB Series) FT-IR spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded at 300, 400 and 500 MHz on a Bruker FT-NMR spectrometers with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in parts per million (ppm) downfield of TMS. Elemental analysis was performed using Elementar Systeme (Vario ELIII) and GC-MS analysis was carried out using Varian 2000 L Single Quadrupole instrument. We have reported only the relevant data for the characterisation of novel compounds synthesised by us.

4.5.2. Starting Materials. All standard reagents were purchased from S. D. Fine Chem. Ltd. and were used as obtained. Dimethyl acetylenedicarboxylate, ethyl propiolate, phenylacetylene and diphenylacetylene were purchased from Sigma-Aldrich and were used as obtained. Solvents were distilled and dried as per requirements.

4.5.2.1. Dibenzoylacetylene: Dibenzoylacetylene was prepared by a known method (72%, mp 109-112 ^{0}C)[60].

4.5.3. Reactions of (Anthracen-9-yl)methylamines with DMAD in Nonpolar Medium.

4.5.3.1. Reactions in Xylene

4.5.3.1.1. Reaction of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a).

To a solution of **1a** (1.88 g, 8 mmol) in dry xylene (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed under nitrogen atmosphere for 48 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:6) of hexane and dichloromethane gave **3** (traces). Further elution with a mixture (1:7) of mixture hexane and dichloromethane gave lepidopterene (**4**) (290 mg, 19%). Further elution with dichloromethane with 1% ethyl acetate gave **2a** in trace amounts.

Compound 2a: (traces); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.49 (6H, s), 3.45 (2H, s), 3.71 (3H, s), 3.82 (3H, s), 5.53 (1H, s), 6.97-7.45 (8H, m, aromatic protons); GC-MS, *m/z* 377 (M^+).

Compound 3: (traces); mp 310-314 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.07 (4H, s), 7.45-8.42 (18H, m, aromatic); Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80; Found: C, 94.22; H, 5.79.

Compound 4: (19%); mp 316-318 ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.90 (4H, d, J = 3.0 Hz), 4.63 (2H, t, J = 2.5 Hz), 6.71-7.34 (16H, m, aromatic); ^{13}C NMR (300 MHz, $CDCl_3$) δ 28.93, 45.58, 54.01, 122.22, 122.35, 122.64, 125.48, 143.15, 143.40; Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80; Found: C, 94.29; H, 5.82. Structure was further confirmed by single crystal analysis using X-ray crystallography.

4.5.3.1.2. Reaction of *N*-((Anthracen-9-yl)methyl)pyrrolidine (1b).

To a solution of **1b** (2.09 g, 8 mmol) in dry xylene (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed under nitrogen atmosphere for 48 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:6) of hexane and dichloromethane gave **3** (traces). Further elution with a mixture (1:7) of mixture hexane and dichloromethane gave lepidopterene (**4**) (310 mg, 20%).

Compound 3: (traces); mp 310-314 ^{0}C.

Compound 4: (20%); mp 316-318 ^{0}C.

4.5.3.1.3. Reaction of *N*-((Anthracen-9-yl)methyl)piperidine (1c).

To a solution of **1c** (2.20 g, 8 mmol) in dry xylene (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed under nitrogen atmosphere for 48 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:6) of hexane and dichloromethane gave **3** (traces). Further elution with a mixture (1:7) of mixture hexane and dichloromethane gave lepidopterene (**4**) (340 mg, 22%).

Compound 3: (traces); mp 310-314 ^{0}C.

Compound 4: (22%); mp 316-318 ^{0}C.

4.5.3.1.4. Reaction of *N*-((Anthracen-9-yl)methyl)hexamethyleneimine (1d).

To a solution of **1d** (2.31 g, 8 mmol) in dry xylene (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed under nitrogen atmosphere

for 48 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:6) of hexane and dichloromethane gave **3** (traces). Further elution with a mixture (1:7) of mixture hexane and dichloromethane gave lepidopterene (**4**) (290 mg, 18%).

Compound 3: (traces); mp 310-314 ^{0}C.

Compound 4: (18%); mp 316-318 ^{0}C.

4.5.3.1.5. Reaction of 9-(*N,N*-Diisopropylaminomethyl)anthracene (1e).

To a solution of **1e** (2.32 g, 8 mmol) in dry xylene (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed under nitrogen atmosphere for 48 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:6) of hexane and dichloromethane gave **3** (traces). Further elution with a mixture (1:7) of mixture hexane and dichloromethane gave lepidopterene (**4**) (250 mg, 16%).

Compound 3: (traces); mp 310-314 ^{0}C.

Compound 4: (16%); mp 316-318 ^{0}C.

4.5.3.1.6. Reaction of 9-(*N*-Methyl-*N*-benzylaminomethyl)anthracene (1f).

To a solution of **1f** (2.48 g, 8 mmol) in dry xylene (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed under nitrogen atmosphere for 48 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:6) of hexane and dichloromethane gave **3** (traces). Further elution with a mixture (1:7) of mixture hexane and dichloromethane gave lepidopterene (**4**) (215 mg, 14%).

Compound 3: (traces); mp 310-314 ^{0}C.

Compound 4: (14%); mp 316-318 ^{0}C.

4.5.3.1.7. Reaction of *N*-((Anthracen-9-yl)methyl)morpholine (1g).

To a solution of **1g** (2.21 g, 8 mmol) in dry xylene (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed under nitrogen atmosphere for 48 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:6) of hexane and dichloromethane gave **3** (traces). Further elution with a mixture (1:7) of mixture hexane and dichloromethane gave lepidopterene (**4**) (340 mg, 22%).

Compound 3: (traces); mp 310-314 ^{0}C.

Compound 4: (22%); mp 316-318 ^{0}C.

4.5.3.1.8. Reaction of 1-((Anthracen-9-yl)methyl)-2-methyl-1*H*-benzo[*d*]-imidazole (1h).

To a solution of **1h** (2.57 g, 8 mmol) in dry xylene (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed under nitrogen atmosphere for 48 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:6) of hexane and dichloromethane gave **3** (traces). Further elution with a mixture (1:7) of mixture hexane and dichloromethane gave lepidopterene (**4**) (190 mg, 12%).

Compound 3: (traces); mp 310-314 ^{0}C.

Compound 4: (12%); mp 316-318 ^{0}C.

4.5.3.2. Reaction of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DMAD in Toluene.

To a solution of **1a** (1.88 g, 8 mmol), in dry toluene (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed under nitrogen atmosphere for 48 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:6) of hexane and dichloromethane gave **3** (traces). Further elution with a mixture (1:7) of mixture hexane and dichloromethane gave lepidopterene (**4**) (230 mg, 15%).

Compound 3: (traces); mp 310-314 ^{0}C.

Compound 4: (15%); mp 316-318 ^{0}C.

4.5.3.3. Reactions of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DMAD in Benzene.

To a solution of **1a** (1.88 g, 8 mmol), in dry benzene (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed under nitrogen atmosphere for 48 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:6) of hexane and dichloromethane gave **3** (traces). Further elution with a mixture (1:7) of mixture hexane and dichloromethane gave Lepidopterene (**4**) (130 mg, 8%).

Compound 3: (traces); mp 310-314 ^{0}C.

Compound 4: (8%); mp 316-318 ^{0}C.

4.5.4. Reactions of (Anthracen-9-yl)methylamines with DMAD in Carboxylic Acids

4.5.4.1. Reactions in Acetic Acid

4.5.4.1.1. Reaction of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a).

To a solution of **1a** (1.88 g, 8 mmol) in glacial acetic acid (10 mL), DMAD (2.00 g, 14 mmol) was added and refluxed for 2 h. Solvent was removed under reduced pressure and the residue was washed with a 5% solution of sodium bicarbonate and extracted with dichloromethane. Organic extracts were combined and dried over $MgSO_4$ and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:8) of hexane and dichloromethane gave **12** (900 mg, 45%). Further elution with a mixture (1:9) of hexane and dichloromethane gave **13** (1.25 g, 40%).

Compound 12: (45%); mp 108-110 ^{0}C; IR ν_{max} (KBr) 1249 cm^{-1}, 1726 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.09 (3H, s); 6.16 (2H, s), 8.05-7.47 (9H, m, aromatic), ^{13}C NMR (300 MHz, $CDCl_3$) δ 21.01, 58.82, 123.94, 125.16, 126.26, 126.75, 129.12, 129.27, 131.18, 131.43, 171.39; GC-MS, *m/z* 250 *(M^+)*, 191 (base peak) and other peaks; Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64; Found: C, 81.51; H, 5.58.

Compound 13: (40%); mp 161-163 ^{0}C; (KBr) 1231 cm^{-1}, 1715 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.13 (3H, s), 3.75 (3H, s), 3.76 (3H, s), 5.44 (2H, s), 5.62 (1H, s), 7.41-7.03 (8H, m, aromatic); GC-MS, *m/z* 392 *(M^+)* and other peaks; Anal. Calcd for $C_{23}H_{20}O_6$: C, 70.40; H, 5.14; Found C, 70.38; H, 5.20.

4.5.4.1.2. Reaction of *N*-((Anthracen-9-yl)methyl)pyrrolidine (1b).

To a solution of **1b** (2.51 g, 8 mmol) in glacial acetic acid (10 mL), DMAD (2.00 g, 14 mmol) was added and refluxed for 2 h. Solvent was removed under reduced pressure and the residue was washed with a 5% solution of sodium bicarbonate and extracted with dichloromethane. Organic extracts were combined and dried over $MgSO_4$ and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:8) of hexane and dichloromethane gave **12** (840 mg, 42%). Further elution with a mixture (1:9) of hexane and dichloromethane gave **13** (1.20 g, 38%).

Compound 12: (42%); mp 108-110 ^{0}C; GC-MS, *m/z* 250 (M^+), 191 (base peak) and other peaks

Compound 13: (38%); mp 161-163 ^{0}C; GC-MS, *m/z* 392 (M^+).

4.5.4.1.3. Reaction of *N*-((Anthracen-9-yl)methyl)piperidine (1c).

To a solution of **1c** (2.20 g, 8 mmol) in glacial acetic acid (10 mL), DMAD (2.00 g, 14 mmol) was added and refluxed for 2 h. Solvent was removed under reduced pressure and the residue was washed with a 5% solution of sodium bicarbonate and extracted with dichloromethane. Organic extracts were combined and dried over $MgSO_4$ and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:8) of hexane and dichloromethane gave **12** (800 mg, 40%). Further elution with a mixture (1:9) of hexane and dichloromethane gave **13** (1.25 g, 40%).

Compound 12: (40%); mp 108-110 ^{0}C; GC-MS, *m/z* 250 (M^+), 191 (base peak) and other peaks

Compound 13: (40%); mp 161-163 ^{0}C; GC-MS, *m/z* 392 *(M^+)*.

4.5.4.1.4. Reaction of *N*-((Anthracen-9-yl)methyl)hexamethyleneimine (1d).

To a solution of **1d** (2.31 g, 8 mmol) in glacial acetic acid (10 mL), DMAD (2.00 g, 14 mmol) was added and refluxed for 2 h. Solvent was removed under reduced pressure and the residue was washed with a 5% solution of sodium bicarbonate and extracted with dichloromethane. Organic extracts were combined and dried over $MgSO_4$ and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:8) of hexane and dichloromethane gave **12** (720 mg, 36%). Further elution with a mixture (1:9) of hexane and dichloromethane gave **13** (1.25 g, 40%).

Compound 12: (36%); mp 108-110 ^{0}C; GC-MS, *m/z* 250 *(M^+)*, 191 (base peak) and other peaks

Compound 13: (40%); mp 161-163 ^{0}C; GC-MS, *m/z* 392 *(M^+)*.

4.5.4.1.5. Reaction of 9-(*N*,*N*-Diisopropylaminomethyl)anthracene (1e).

To a solution of **1e** (2.32 g, 8 mmol) in glacial acetic acid (10 mL), DMAD (2.00 g, 14 mmol) was added and refluxed for 2 h. Solvent was removed under reduced pressure and the residue was washed with a 5% solution of sodium bicarbonate and extracted with dichloromethane. Organic extracts were combined and dried over $MgSO_4$ and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:8) of hexane and dichloromethane gave **12** (640 mg, 32%). Further elution with a mixture (1:9) of hexane and dichloromethane gave **13** (880 mg, 28%).

Compound 12: (32%); mp 108-110 ^{0}C; GC-MS, *m/z* 250 *(M^+)*, 191 (base peak) and other peaks

Compound 13: (28%); mp 161-163 ^{0}C; GC-MS, *m/z* 392 *(M^+)*.

4.5.4.1.6. Reaction of 9-(*N*-Methyl-*N*-benzylaminomethyl)anthracene (1f).

To a solution of **1d** (2.48 g, 8 mmol) in glacial acetic acid (10 mL), DMAD (2.00 g, 14 mmol) was added and refluxed for 2 h. Solvent was removed under reduced pressure and the residue was washed with a 5% solution of sodium bicarbonate and extracted with dichloromethane. Organic extracts were combined and dried over $MgSO_4$ and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:8) of hexane and dichloromethane gave **12** (600 mg, 30%). Further elution with a mixture (1:9) of hexane and dichloromethane gave **13** (790 mg, 25%).

Compound 12: (30%); mp 108-110 ^{0}C; GC-MS, *m/z* 250 *(M^+)*, 191 (base peak) and other peaks

Compound 13: (25%); mp 161-163 ^{0}C; GC-MS, *m/z* 392 *(M^+)*.

4.5.4.1.7. Reaction of *N*-((Anthracen-9-yl)methyl)morpholine (1g).

To a solution of **1g** (2.21 g, 8 mmol) in glacial acetic acid (10 mL), DMAD (2.00 g, 14 mmol) was added and refluxed for 2 h. Solvent was removed under reduced pressure and the residue was washed with a 5% solution of sodium bicarbonate and extracted with dichloromethane. Organic extracts were combined and dried over $MgSO_4$ and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:8) of hexane and dichloromethane gave

12 (960 mg, 48%). Further elution with a mixture (1:9) of hexane and dichloromethane gave **13** (1.37 g, 42%).

Compound 12: (48%); mp 108-110 ^{0}C; GC-MS, *m/z* 250 *(M^+)*, 191 (base peak) and other peaks

Compound 13: (42%); mp 161-163 ^{0}C; GC-MS, *m/z* 392 *(M^+)*.

4.5.4.1.8. Reaction of 1-((Anthracen-9-yl)methyl)-2-methyl-1*H*-benzo[*d*]-imidazole (1h).

To a solution of **1h** (2.57 g, 8 mmol) in glacial acetic acid (10 mL), DMAD (2.00 g, 14 mmol) was added and refluxed for 2 h. Solvent was removed under reduced pressure and the residue was washed with a 5% solution of sodium bicarbonate and extracted with dichloromethane. Organic extracts were combined and dried over $MgSO_4$ and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:8) of hexane and dichloromethane gave **12** (400 mg, 20%). Further elution with a mixture (1:9) of hexane and dichloromethane gave **13** (690 mg, 22%).

Compound 12: (20%); mp 108-110 ^{0}C; GC-MS, *m/z* 250 *(M^+)*, 191 (base peak) and other peaks

Compound 13: (22%); mp 161-163 ^{0}C; GC-MS, *m/z* 392 *(M^+)*.

4.5.4.2. Reaction of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DMAD in propionic acid.

To a solution of **1a** (2.31 g, 8 mmol) in propionic acid (10 mL), DMAD (2.00 g, 14 mmol) was added and refluxed for 2 h. Solvent was removed under reduced pressure and the residue was washed with a 5% solution of sodium bicarbonate and extracted with dichloromethane. Organic extracts were

combined and dried over $MgSO_4$ and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:6) of hexane and dichloromethane gave **15** (950 mg, 45%). Further elution with a mixture (1:8) of hexane and dichloromethane gave **16** (1.30 g, 40%).

Compound 15: (45%); mp 99-102 ^{0}C; IR ν_{max} (KBr) 1257 cm^{-1}, 1732 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.12-1.16 (3H, t, J = 7.5 Hz), 2.32-2.38 (2H, m), 6.15 (2H, s), 7.47- 8.51 (9H, m, aromatic); ^{13}C NMR (300 MHz, $CDCl_3$) δ 7.2, 25.02, 58.81, 124.20, 125.18, 126.22, 126.76, 129.14, 129.25, 131.29, 133.43, 172.46; GC-MS, *m/z* 265 (M^+), 191 (base peak) and other peaks; Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10; Found: C, 81.75; H, 6.08.

Compound 16: (40%); mixture mp 150-152 ^{0}C ; (KBr) 1241 cm^{-1}, 1728 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.17-1.21 (3H, m), 2.37-2.43 (2H, m), 3.74 (3H, s), 3.76 (3H, s), 5.45 (2H, s), 5.62 (1H, s), 7.03-7.41 (8H, m, aromatic); Anal. Calcd for $C_{24}H_{24}O_6$: C, 70.92; H, 5.46; Found C, 71.86; H, 5.62.

4.5.4.3. Reactions of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DMAD in Trifluoroacetic Acid

To a solution of **1a** (1.88 g, 8 mmol) in trifluoroacetic acid (10 mL), DMAD (2.00 g, 14 mmol) was added and refluxed for 8 h. Solvent was removed under reduced pressure and the residue obtained was diluted with dichloromethane. The precipitate obtained was filtered and washed with dichloromethane. Organic extracts were combined and dried over $MgSO_4$ and concentrated. TLC of the organic extract showed no observable spots. The precipitate obtained was characterised to be compound **17**.

Compound 17: (92%); 216-218 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.86 (6H, s), 5.40 (2H, s), 7.60-8.84 (9H, m, aromatic); ^{13}C NMR (400 MHz, $CDCl_3$) δ 27.58, 58.76, 123.71, 123.99, 125.09, 126.59, 127.80, 129.10, 131.09, 131.44.

4.5.4.4. Reaction of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DMAD in Formic Acid

To a solution of **1a** (1.88 g, 8 mmol) in formic acid (10 mL), DMAD (2.00 g, 14 mmol) was added and refluxed for 8 h. Solvent was removed under reduced pressure and the residue obtained was diluted with dichloromethane. The precipitate obtained was filtered and washed with dichloromethane. Organic extracts were combined and dried over $MgSO_4$ and concentrated. TLC of the organic extract showed no observable spots. The precipitate obtained was characterised to be compound **18**.

Compound 18: (94%); 179-182 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.86 (6H, s), 5.40 (2H, s), 7.60-8.84 (9H, m, Aromatic); ^{13}C NMR (400 MHz, $CDCl_3$) δ 25.58, 58.74, 123.72, 123.81, 125.16, 126.61, 127.80, 129.10, 131.01, 132.62.

4.5.5. Reactions of Salts of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DMAD.

4.5.5.1. Reactions of Hydrochloride of 9-(*N,N*-Dimethylaminomethyl)-anthracene (19)[11] with DMAD.

A mixture of **19** (2.16 g, 8 mmol) and DMAD (2.00 g, 14 mmol) was taken in a sealed ampule and heated at 120 ^{0}C for 6 h. The reaction mixture was extracted with 10 mL of dichloromethane. A precipitate obtained was filtered and washed with dichloromethane and was found to be unchanged **19**. Organic extracts were combined and dried over $MgSO_4$ and concentrated. TLC of the organic extract showed no observable spots.

4.5.5.2. Reactions of BF3 salt of 9-(*N,N*-Dimethylaminomethyl)anthracene (20) with DMAD.

A mixture of **20** (2.33 g, 8 mmol) and DMAD (2.00 g, 14 mmol) was taken in a sealed ampule and heated at 120 ^{0}C 6 h. The reaction mixture is extracted with 10 mL of dichloromethane. A precipitate obtained was filtered and washed with dichloromethane and was found to be unchanged **20**. Organic extracts were combined and dried over $MgSO_4$ and concentrated. TLC of the organic extract showed no observable spots.

4.5.6. Reactions of (Anthracen-9-yl)methylamines with DMAD in Alcohols

4.5.6.1. Reactions of DMAD in Methanol

4.5.6.1.1. Reaction of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a).

To a solution of **1a** (1.88 g, 8 mmol) in methanol (10 mL), DMAD (2.00 g, 12 mmol) was added and refluxed for 8 h. Solvent was removed under reduced pressure and the residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:7) of hexane and dichloromethane gave compound **21** (1.21 g, 68%). Further elution with dichloromethane gave **10a**[57] (970 mg, 65%).

Compound 10a: (65%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80 (6H, s), 3.56 (6H, s), 4.51 (1H, s); ^{13}C NMR (400 MHz, $CDCl_3$) δ 39.74, 50.71, 52.85, 84.81, 155.23, 168.06; GC-MS, *m/z* 187 *(M^+)* and other peaks; Anal. Calcd for $C_8H_{13}NO_4$: C, 51.33; H, 7.00; N, 7.48; Found: C, 51.31; H, 7.02; N, 7.51.

Compound 21: (68%); mp 88-90 ^{0}C; IR ν_{max} (KBr) 1192 cm^{-1} (OC_2H_5), ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.53 (3H, s), 5.42 (2H, s), 7.44-8.45 (9H, m, aromatic); ^{13}C NMR (400 MHz, $CDCl_3$) δ 58.42, 66.59, 124.32, 125.11, 126.26, 128.50, 129.02, 121.07, 131.58, 134.03; GC-MS, *m/z* 222 *(M^+)* and

other peaks; Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35; Found: C, 86.38; H, 6.31.

4.5.6.1.2. Reaction of *N*-((Anthracen-9-yl)methyl)pyrrolidine (1b).

To a solution of **1b** (2.51 g, 8 mmol) in methanol (10 mL), DMAD (2.00 g, 12 mmol) was added and refluxed for 8 h. Solvent was removed under reduced pressure and the residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:7) of hexane and dichloromethane gave compound **21** (1.15 g, 65%). Further elution with dichloromethane gave **10b** (1.02 g, 60%).[61]

Compound 10b: (60%); GC-MS, *m/z* 213 (M^+) and other peaks; Anal. Calcd for $C_{10}H_{15}NO_4$: C, 56.33; H, 7.09; N, 6.57; Found: C, 56.41; H, 7.12; N, 6.60.

Compound 21: (65%); mp 88-90 ^{0}C; GC-MS, *m/z* 222 (M^+) and other peaks.

4.5.6.1.3. Reaction of *N*-((Anthracen-9-yl)methyl)piperidine (1c).

To a solution of **1c** (2.51 g, 8 mmol) in methanol (10 mL), DMAD (2.00 g, 12 mmol) was added and refluxed for 8 h. Solvent was removed under reduced pressure and the residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:7) of hexane and dichloromethane gave compound **21** (1.07 g, 60%). Further elution with dichloromethane gave **10c**[62] (1.12 g, 62%).

Compound 10c: (62%); GC-MS, *m/z* 227 (M^+) and other peaks; Anal. Calcd for $C_{11}H_{17}NO_4$: C, 58.14; H, 7.54; N, 6.16; Found: C, 58.17; H, 7.61; N, 6.20.

Compound 21: (60%); mp 88-90 ^{0}C; GC-MS, *m/z* 222 (M^+) and other peaks.

4.5.6.1.4. Reaction of *N*-((Anthracen-9-yl)methyl)hexamethyleneimine (1d).

To a solution of **1d** (2.51 g, 8 mmol) in methanol (10 mL), DMAD (2.00 g, 12 mmol) was added and refluxed for 8 h. Solvent was removed under reduced pressure and the residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:7) of hexane and dichloromethane gave compound **21** (1.03 g, 58%). Further elution with dichloromethane gave **10d** (1.06 g, 55%).

Compound 10d: (55%); GC-MS, *m/z* 241 (M^+) and other peaks; Anal. Calcd for $C_{12}H_{19}NO_4$: C, 59.73; H, 7.94; N, 5.81; Found: C, 59.75; H, 7.92; N, 5.79.

Compound 21: (58%); mp 88-90 ^{0}C; GC-MS, *m/z* 222 (M^+) and other peaks.

4.5.6.1.5. Reaction of 9-(*N,N*-Diisopropylaminomethyl)anthracene (1e).

To a solution of **1e** (2.51 g, 8 mmol) in methanol (10 mL), DMAD (2.00 g, 12 mmol) was added and refluxed for 8 h. Solvent was removed under reduced pressure and the residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:7) of hexane and dichloromethane gave compound **21** (890 mg, 50%). Further elution with dichloromethane gave **10e**[63] (910 mg, 47%).

Compound 10e: (47%); GC-MS, *m/z* 243 (M^+) and other peaks; Anal. Calcd for $C_{12}H_{21}NO_4$: C, 59.24; H, 8.70; N, 5.76; Found: C, 59.21; H, 8.64; N, 5.73.

Compound 21: (50%); mp 88-90 ^{0}C; GC-MS, *m/z* 222 (M^+) and other peaks.

4.5.6.1.6. Reaction of 9-(*N*-Methyl-*N*-benzylaminomethyl)anthracene (1f).

To a solution of **1f** (2.51 g, 8 mmol) in methanol (10 mL), DMAD (2.00 g, 12 mmol) was added and refluxed for 8 h. Solvent was removed under reduced

pressure and the residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:7) of hexane and dichloromethane gave compound **21** (1.15 g, 72%). Further elution with dichloromethane gave **10f**[64] (1.41 g, 67%).

Compound 10f: (67%); GC-MS, *m/z* 263 (M^+) and other peaks; Anal. Calcd for $C_{14}H_{17}NO_4$: C, 63.87; H, 6.51; N, 5.32; Found: C, 63.85; H, 6.50; N, 5.35.

Compound 21: (72%); mp 88-90 ^{0}C; GC-MS, *m/z* 222 (M^+) and other peaks.

4.5.6.1.7. Reaction of *N*-((Anthracen-9-yl)methyl)morpholine (1g).

To a solution of **1g** (2.51 g, 8 mmol) in methanol (10 mL), DMAD (2.00 g, 12 mmol) was added and refluxed for 8 h. Solvent was removed under reduced pressure and the residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:7) of hexane and dichloromethane gave compound **21** (1.37 mg, 77%). Further elution with dichloromethane gave **10g**[65] (1.32 mg, 72%).

Compound 10g: (72%); GC-MS, *m/z* 229 (M^+) and other peaks; Anal. Calcd for $C_{10}H_{15}NO_5$: C, 52.40; H, 6.60; N, 6.11; Found: C, 52.43; H, 6.57; N, 6.16.

Compound 21: (77%); mp 88-90 ^{0}C; GC-MS, *m/z* 222 (M^+) and other peaks.

4.5.6.1.8. Reaction of 1-((Anthracen-9-yl)methyl)-2-methyl-1*H*-benzo[*d*]-imidazole (1h).

To a solution of **1h** (2.51 g, 8 mmol) in methanol (10 mL), DMAD (2.00 g, 12 mmol) was added and refluxed for 8 h. Solvent was removed under reduced pressure and the residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:7) of hexane and dichloromethane gave compound **21** (750 mg, 42%). Further elution with dichloromethane gave **10h**[66] (830 mg, 38%).

Compound 10h: (38%); GC-MS, *m/z* 274 (M^+) and other peaks; Anal. Calcd for $C_{14}H_{14}N2O_4$: C, 61.31; H, 5.14; N, 10.21; Found: C, 61.32; H, 5.15; N, 10.23.

Compound 21: (42%); mp 88-90 ^{0}C; GC-MS, *m/z* 222 (M^+) and other peaks.

4.5.6.2. Reaction of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DMAD in Ethanol

To a solution of **1a** (1.88 g, 8 mmol) in ethanol (10 mL), DMAD (2.00 g, 12 mmol) was added and refluxed for 8 h. Solvent was removed under reduced pressure and the residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:6) of hexane and dichloromethane gave compound **21a**[67] (1.40 mg, 74%). Further elution with dichloromethane gave **10a** (1.04 mg, 70%).

Compound 10a: (70%); GC-MS, *m/z* 187 (M^+) and other peaks.

Compound 21a: (74%); mp 70-74 ^{0}C; IR ν_{max} (KBr) 1084 cm^{-1} (OC_2H_5); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (2H, m), 1.28 (3H, t, J = 7.8 Hz), 3.24 (2H, s), 7.28-8.36 (9H, m, aromatic); GC-MS, *m/z* 236 (M^+) and other peaks; Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82; Found: C, 86.45; H, 6.77.

4.5.6.3. Reaction of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DMAD in Allyl alcohol

To a solution of **1a** (1.88 g, 8 mmol) in allylalcohol (10 mL), DMAD (2.00 g, 12 mmol) was added and refluxed for 8 h. Solvent was removed under reduced pressure and the residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:7) of hexane and dichloromethane gave compound **21b**[68] (1.62 g, 82%). Further elution with dichloromethane gave **10a** (1.12 g, 75%).

Compound 10a: (75%); GC-MS, *m/z* 187 (M^+) and other peaks.

Compound 21b: (82%); mp 50-55 ^{0}C; IR ν_{max} (KBr) 1049 cm^{-1}, 1123 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.26 (2H, d), 5.31-5.54 (4H, m) 6.01-6.15 (1H, m,), 7.32-8.54 (9H, m, aromatic); ^{13}C NMR (300 MHz, $CDCl_3$) δ 29.32, 46.91, 64.87, 66.76, 118.34, 125.10, 125.66, 126.97, 129.10, 129.72, 131.87, 135.70; MS, *m/z* 248 (M^+), and other peaks. Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 87.11; H, 6.45.

4.5.6.4. Reactions 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DMAD in *i*-Propanol

To a solution of **1a** (1.88 g, 8 mmol) in *i*-propanol (10 mL), DMAD (2.00 g, 12 mmol) was added and refluxed for 8 h. Solvent was removed under reduced pressure and the residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:5) of hexane and dichloromethane gave compound **21c** (1.20 g, 60%). Further elution with dichloromethane gave **10a** (870 mg, 58%).

Compound 10a: (58%); GC-MS, *m/z* 187 (M^+) and other peaks.

Compound 21c: (60%); mp 84-86 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34-1.36 (2H, d, J = 8.0 Hz); 3.92-4.00 (3H, m), 5.47 (2H, s), 7.45-8.41 (9H, m, aromatic); ^{13}C NMR (400 MHz, $CDCl_3$) δ 21.39, 60.51, 66.59, 124.36, 125.16, 125.66, 126.93, 129.41, 129.73, 131.58, 135.79; GC-MS, *m/z* 250 (M^+) and other peaks; Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.44; Found: C, 86.28; H, 7.48.

4.5.6.5. Reactions of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DMAD in *t*-Butanol

To a solution of **1a** (1.88 g, 8 mmol) in t-butanol (10 mL), DMAD (2.00 g, 12 mmol) was added and refluxed for 8 h. Solvent was removed under reduced pressure and the residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:8) of hexane and dichloromethane gave compound **21d** (840 mg, 40%). Further elution with dichloromethane gave **10a** (670 mg, 45%).

Compound 10a: (45%); GC-MS, *m/z* 187 (M^+) and other peaks.

Compound 21d: (40%); mp 67-71 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (9H, s); 5.37 (2H, s), 7.44-8.42 (9H, m, aromatic); ^{13}C NMR (400 MHz, $CDCl_3$) δ 29.69, 56.60, 73.88, 122.55, 124.38, 124.81, 125.12, 125.93, 127.42, 129.32, 131.01; GC-MS, *m/z* 264 (M^+) and other peaks; Anal. Calcd for $C_{19}H_{20}O$: C, 86.32; H, 7.63; Found: C, 68.30; H, 7.59.

4.5.6.6. Reaction of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DMAD in 1-Propanol

To a solution of **1a** (1.88 g, 8 mmol) in 1-propanol (10 mL), DMAD (2.00 g, 12 mmol) was added and refluxed for 2 h. Solvent was removed under reduced pressure and 15 mL of dichloromethane was added to the residue obtained. TLC of the reaction mixture indicated a complex mixture. GCMS of the reaction mixture showed the presence of **21e** and **10a** along with several isomeric impurities.

Compound 10a: GC-MS, *m/z* 187 (M^+) and other peaks.

Compound 21e: GC-MS, *m/z* 191 (base peak), 250 (M^+).

4.5.6.7. Reaction of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DMAD in 1-Butanol

To a solution of **1a** (1.88 g, 8 mmol) in 1-butanol (10 mL), DMAD (2.00 g, 12 mmol) was added and refluxed for 2 h. Solvent was removed under reduced pressure and 15 mL of dichloromethane was added to the residue obtained. TLC of the reaction mixture indicated a complex mixture. GCMS of the reaction mixture showed the presence of **21f** and **10a** along with several isomeric impurities.

Compound 10a: GC-MS, *m/z* 187 (M^+) and other peaks.

Compound 21f: GC-MS, *m/z* 191 (base peak), 264 (M^+).

4.5.7. Reactions of 9-(*N,N*-Dimethylaminomethyl)anthracene with DMAD in Polar Aprotic Medium.

4.5.7.1. Reaction of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DMAD in Acetonitrile.

To a solution of **1a** (1.88 g, 8 mmol), in dry acetonitrile (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed 50 h. GC-MS of the reaction mixture showed the presence of trace amount of **10a**. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:99) of ethyl acetate and dichloromethane gave **1a** (1.56 g) and further elution gave polymeric material.

4.5.7.2. Reactions of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DMAD in 1,4-Dioxan.

To a solution of **1a** (1.88 g, 8 mmol), in 1,4-Dioxan (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed 50 h. GC-MS of the

reaction mixture showed the presence of unchanged **1a**. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:99) of ethyl acetate and dichloromethane gave **1a** (1.75 g) and further elution gave polymeric material.

4.5.7.3. Reactions of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DMAD in DMF.

To a solution of **1a** (1.88 g, 8 mmol), in dry DMF (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed 50 h. GC-MS of the reaction mixture showed the presence of unchanged **1a** and trace amount of **10a**. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:99) of ethyl acetate and dichloromethane gave **1a** (1.68 g) and further elution gave polymeric material.

4.5.7.4. Reactions of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DMAD in Chlorobenzene

To a solution of **1a** (1.88 g, 8 mmol), in Chlorobenzene (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed 50 h. GC-MS of the reaction mixture showed the presence of unchanged **1a** and trace amount of **10a**. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:99) of ethyl acetate and dichloromethane gave **1a** (1.80 g) and further elution gave polymeric material.

4.5.8. Reactions of (Anthracen-9-yl)methylamine with Ethyl Propiolate

4.5.8.1. Reactions of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with Ethyl Propiolate in Xylene

To a solution of **1a** (1.88 g, 8 mmol), in dry xylene (10 mL), Ethyl propiolate (1.16 g, 14 mmol) was added and the mixture was refluxed under nitrogen atmosphere for 48 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:6) of hexane and dichloromethane gave **3** (traces). Further elution with a mixture (1:7) of hexane and dichloromethane gave lepidopterene (**4**) (610 mg, 10%).

Compound 3: (traces); mp 310-314 ^{0}C.

Compound 4: (10%); mp 316-318 ^{0}C.

4.5.8.2. Reactions of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with Ethyl Propiolate in Acetic Acid

To a solution of **1a** (1.88 g, 8 mmol) in glacial acetic acid (10 mL), ethyl propiolate (1.16 g, 14 mmol) was added and refluxed for 2 h. Solvent was removed under reduced pressure and the residue was washed with a 5% solution of sodium bicarbonate and extracted with dichloromethane. Organic extracts were combined and dried over $MgSO_4$ and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:8) of hexane and dichloromethane gave **12** (840 mg, 42%).

Compound 12: (42%); mp 108-110 ^{0}C; GC-MS, *m/z* 250 (M^+), 191 (base peak) and other peaks.

4.5.8.3. Reactions of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with Ethyl propiolate in Methanol

To a solution of **1a** (1.88 g, 8 mmol) in methanol (10 mL), ethyl propiolate (1.16 g, 14 mmol) was added and refluxed for 8 h. Solvent was removed under reduced pressure and the residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:7) of hexane and dichloromethane gave compound **21** (780 mg, 45%). Further elution with dichloromethane gave **24**[59] (480 mg, 42%).

Compound 21: (45%); mp 88-90 ^{0}C; GC-MS, *m/z* 222 (M^+) and other peaks.

Compound 24: (42%); GC-MS, *m/z* 143 (M^+) and other peaks; Anal. Calcd for $C_7H_{13}NO_2$: C, 58.72; H, 9.15; N, 9.78; Found: C, 58.72; H, 9.15; N, 9.78.

4.5.9. Reactions of 9-(*N,N*-Dimethylaminomethyl)anthracene with DBA

4.5.9.1. Reactions of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DBA in Xylene

To a solution of **1a** (1.88 g, 8 mmol), in dry xylene (10 mL), DBA (3.28 g, 14 mmol) was added and the mixture was refluxed under nitrogen atmosphere for 48 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:6) of hexane and dichloromethane gave **3** (traces). Further elution with a mixture (1:7) of mixture hexane and dichloromethane gave lepidopterene (**4**, 920 mg, 15%). Further elution with a mixture (1:99) of ethyl acetate and dichloromethane gave **25** (1.95 mg, 52%).

Compound 3: (traces); mp 310-314 ^{0}C.

Compound 4: (15%); mp 316-318 ^{0}C.

Compound 25: (52%); mp 148-151 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94 (6H, s), 3.74 (2H, s), 5.41 (1H, s), 7.05-7.45 (18H, m, aromatic); ^{13}C NMR (300 MHz, $CDCl_3$) δ 44.24, 50.58, 52.73, 60.12, 121.14, 123.14,123.20,124.24, 124.64, 126.48, 127.27, 127.54, 128.71, 128.90, 130.51, 132.32, 136.61, 137.58, 145.88, 145.97, 155.10, 194.35; Anal. Calcd for $C_{33}H_{27}NO_2$: C, 84.41; H, 5.80; N, 2.98; Found: C, 84.40; H, 5.78; N, 2.96.

4.5.9.2. Reactions of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DBA in Acetic acid

To a solution of **1a** (1.88 g, 8 mmol) in glacial acetic acid (10 mL), DBA (3.28 g, 14 mmol) was added and refluxed for 2 h. Solvent was removed under reduced pressure and the residue was washed with a 5% solution of sodium bicarbonate and extracted with dichloromethane. Organic extracts were combined and dried over $MgSO_4$ and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:8) of hexane and dichloromethane gave **12** (840 mg, 42%).

Compound 12: (42%); mp 108-110 ^{0}C; GC-MS, *m/z* 250 *(M^+)*, 191 (base peak) and other peaks.

4.5.9.3. Reactions of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with DBA in Methanol

To a solution of **1a** (1.88 g, 8 mmol) in methanol (10 mL), DBA (3.28 g, 12 mmol) was added and refluxed for 8 h. Solvent was removed under reduced pressure and the residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:7) of hexane and dichloromethane gave compound **21** (780 mg, 45%). Further elution with dichloromethane gave **27**[69] (940 mg, 42%).

Compound 21: (45%); mp 88-90 ^{0}C; GC-MS, *m/z* 222 (M^+) and other peaks.

Compound 27: (42%); mp 92-94 ^{0}C; GC-MS, *m/z* 279 (M^+) and other peaks; Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01; Found: C, 77.45; H, 6.21; N, 5.12.

4.5.10. Reactions of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with Diphenylacetyene

To a solution of **1a** (1.88 g, 8 mmol), in o-Dichlorobenzene (10 mL), Diphenylacetylene (2.28 g, 14 mmol) was added and the mixture was refluxed under nitrogen atmosphere for 96 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with hexane-dichloromethane mixture in the ratio 1:4 gave polymer of diphenylacetylene (traces). Further elution with a mixture (1:7) of mixture hexane and dichloromethane gave **28** (130 mg, 4%). Further elution with a mixture (1:99) of ethyl acetate and dichloromethane gave unchanged **1a** (1.54 g, 81%).

Compound 28: (4%); mp 72-74 ^{0}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.64 (3H, s), 2.65 (3H, s), 4.51(2H,s), 4.89 (1H, s), 6.81-7.82 (18H, m, aromatic); ^{13}C NMR (300 MHz, $CDCl_3$) δ 45.04, 55.11, 55.87, 57.91, 121.67, 123.53,125.41,125.80, 127.15, 127.52, 127.94, 128.73, 129.71, 143.12; Anal. Calcd for $C_{31}H_{27}N$: C, 90.03; H, 6.58; N, 3.39; Found: C, 90.11; H, 6.60; N, 3.36.

4.5.11. Reaction of 9-(*N,N*-Dimethylaminomethyl)anthracene (1a) with Phenylacetylene

To a solution of **1a** (1.88 g, 8 mmol), in *o*-dichlorobenzene (10 mL), Phenylacetylene (2.28 g, 14 mmol) was added and the mixture was refluxed

under nitrogen atmosphere for 120 h. GCMS of the reaction mixture indicated the presence of unchanged **1a** and traces of **30**. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:99) of ethyl acetate and dichloromethane gave unchanged **1a** (1.76 g).

Compound 30: GC-MS, *m/z* 337 (M^+).

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Chapter - 5

SYNTHESIS AND REACTIONS OF (ANTHRACEN-9-YL)METHYLSULPHANES WITH DMAD

5.1. Abstract

As an extension to our studies on electron transfer reactions with (anthracen-9-yl)methylamines, we synthesised a few related (anthracen-9-yl)methylsulphanes and examined their solvent dependent reaction with a reactive acetylene like DMAD. This chapter deals with our efforts on the synthesis of anthracenes appended with alkyl sulphides that would serve as potential donors for electron transfer reactions as well as Michael type additions and Diels-Alder reactions with suitable electron deficient acetylenes.

5.2. Introduction

Our investigations on the solvent dependent reactions of anthracene appended tertiary amines with several acetylenes lead us to a question - Will any other electron donor system appended anthracenes give similar chemistry in these reactions? A suitable electron donor system for vindication of this proposal is organosulphur compounds that are known for their diverse chemistry.[1-8] Sulphur compounds are well known for their radical chemistry under thermal and photochemical conditions.[9-17] Sulphur-centered radicals and radical cations formed from thioethers are highly reactive. It is reported that thioethers are ideal precursors for sulphur-centered radical cations that can

be used for probing mechanisms of electron transfer quenching of excited states as well as for monitoring the fate of the sulphur radicals.[1-18] Charge-transfer processes involving organosulphur compounds are of particular interest in biology and chemistry because transient sulphide radical ions can alter or protect the functional properties of enzymatic complexes or proteins.[4-8] Photoexcited organic sulphides undergo different responses which can lead to bond scissions or ionisation channels. The primary processes triggered by UV excitation of liquid organic sulphides correspond to S-S or C-S bond scissions to yield methylthiyl radical or thioformaldehyde.[19-22]

Sulphur analogues of alcohols are called 'thiols' or 'mercaptans', and ether analogues are called 'sulphides' or 'sulphanes'. The chemical behaviour of thiols and sulphides contrasts that of alcohols and ethers in some important ways. In many ways, the reactivity pattern exhibited by these sulphur analogues resembles those of the corresponding amines. Since hydrogen sulphide (H_2S) is a much stronger acid than water, thiols are stronger acids than equivalent alcohols. Thiols, upon reaction with alkyl halides in presence of a strong nonnucleophilic base give the corresponding sulphanes. Thiolate conjugate bases are easily formed, and have proven to be excellent nucleophiles in S_N2 reactions of alkyl halides and tosylates. Similarly, sulphides react with alkyl halides to give ternary sulphonium salts in the same manner that 3°-amines are alkylated to quaternary ammonium salts. Like amines, these sulphur-containing molecules participate in single electron transfer processes as well.

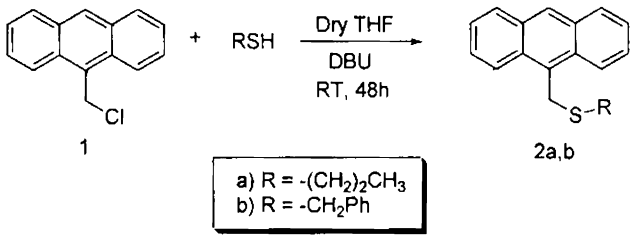
We designed systems with a thioalkyl moiety linked to an anthracene ring through a spacer analogous to the (anthrace-9-yl)methylamines discussed in previous chapters. We employed simple base catalysed nucleophilic substitution reactions on alkyl halides with suitable thiols to achieve the target

molecules. In this chapter we congregate the synthetic aspects of these thioalkyl substituted anthracene compounds and their reactions with dimethyl acetylenedicarboxylate (DMAD) in different solvents.

5.3. Results and Discussion

5.3.1. Preparation of (Anthracen-9-yl)methylsulphanes

Our idea was to synthesise sulphur analogues of (anthracen-9-yl)methylamines and we considered simple analogues sulphane derivatives such as **2a** and **2b**. The selection of the substrates was based on the ready availability of the required thiols. We employed base catalysed nucleophilic substitution reactions on 9-chloromethylanthracene (**1**) with suitable thiols to access the target molecules (Scheme 1). The reaction was conducted in dry tetrahydrofuran (THF) employing 1-propanethiol and benzyl thiol to obtain the corresponding derivatives **2a** and **2b**, respectively. A strong, nonnucleophilic base such as DBU was used to generate the thiolate nucleophile from the thiol and to scavenge HCl. The reaction took place in moderate yields.



Scheme 1

The structure of **2a,b** was established on the basis of analytical results and spectral data. The UV spectra of **2a,b** were dominated by absorption due to the anthracene component present in them. ^{1}H NMR spectra of these compounds were in agreement with the expected structure and they exhibited

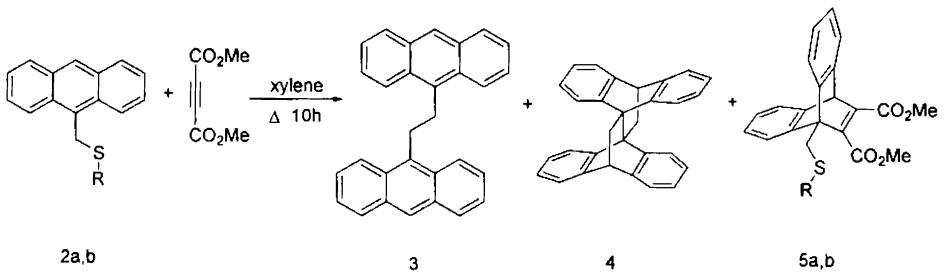
acceptable elemental analysis and mass spectral data. The analytical and spectral data of **2b** was identical to those reported in literature.[23] Thus, we were able to synthesise (anthracen-9-yl)methylsulphanes **2a** and **2b**, which are potential substrates for the study of solvent dependent reactions with DMAD.

(Anthracen-9-yl)methylamines synthesised by us showed dramatic solvent dependence in their reactions with various acetylenes involving electron transfer reactions and Michael-type additions etc. The purpose of our present study is to investigate the role of a sulphane moiety in the (anthracen-9-yl)methylsulphanes **2a-b** in their reaction with DMAD. The observations here were comparable to the results obtained in the case of (anthracen-9-yl)methylamines. Herein we present a detailed account of these reactions and analysis of the results obtained in these reactions.

5.3.2. Reactions of (Anthracen-9-yl)methylsulphanes with DMAD

5.3.2.1. Reactions in Non-polar Solvents

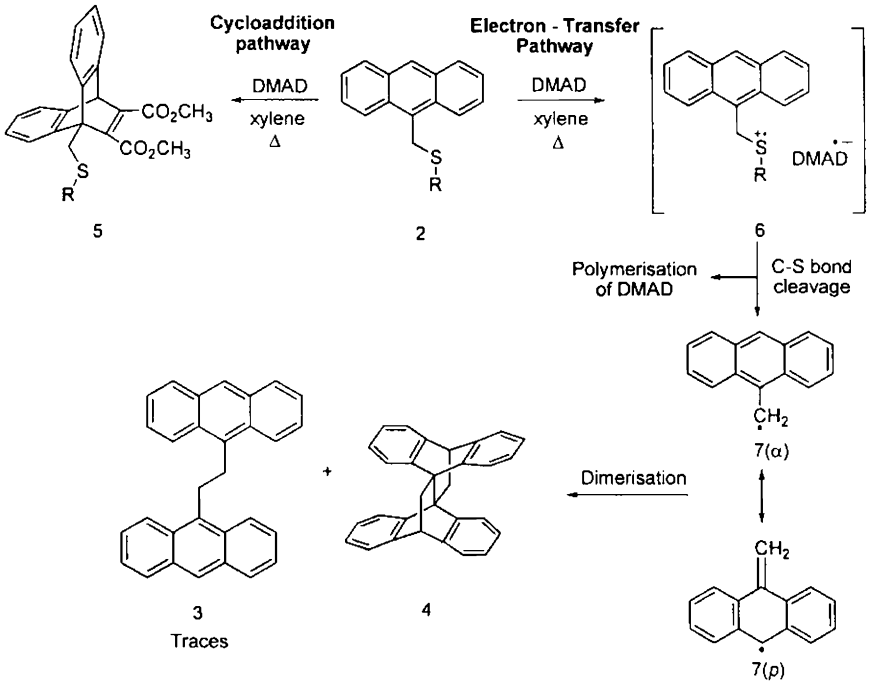
When a mixture of ((anthracen-9-yl)methyl)(propyl)sulphane (**2a**) and DMAD was refluxed in dry xylene for 10 hour, tetrabenzotetracyclo-tetradecatetraene or lepidopterene (**4**) was formed in moderate yields (35%) along with 1,2-bis(9-anthracenyl)ethane (**3**) as a minor product(<5%) and the Diels-Alder adduct **5** in appreciable yield (42%) (Scheme 2). The extent of acetylenic polymerisation in this reaction was less when compared to the reactions of amines presented in Chapter 4. Unlike with amines, the expected Diels-Alder adducts were formed in good yields. However, formation of products such as **3** and **4** indicates the concurrent occurrence of a competing electron transfer pathway in the reaction. Similar results were observed when the reaction was repeated with **2b**.



2a,b 3 4 5a,b

Scheme 2

As in the case of (anthracen-9-yl)methylamines, we propose that the reaction takes place through the formation of a radical ionpair **6** through a single electron transfer from the sulphane moiety to DMAD, followed by C-S bond cleavage generating the 9-anthracenemethyl radical **7** (Scheme 3). There are reports of C-S bond cleavage in organosulphur compounds including sulphanes under thermal and photochemical conditions.[9-12,24,25] The formation of lepidopterene (**4**) and 1,2-bisanthracenenylethane (**3**) from 9-anthracenemethyl radical (**7**) is explained in Chapter 4. Formation of Diels-Alder adduct in major yields indicates that the cycloaddition pathway is important with these systems. Hence, in the case of (anthracen-9-yl)methylsulphanes, both cycloaddition as well as electron transfer reaction pathways are equally favoured.



Scheme 3

Reactions involving sulphanes were cleaner and faster than those with (anthracen-9-yl)methylamines. In this case, **3** and **4** were formed in better yields in comparison with the reactions of (anthracen-9-yl)methylamines along with the formation of the cycloadduct **5a** in substantial amount. Dimerisation of arylmethyl radicals formed from sulphanes under photochemical conditions has literature precedence.[24] Formation of the cycloadduct **5a** was confirmed by ^{1}H NMR spectral and analytical data.

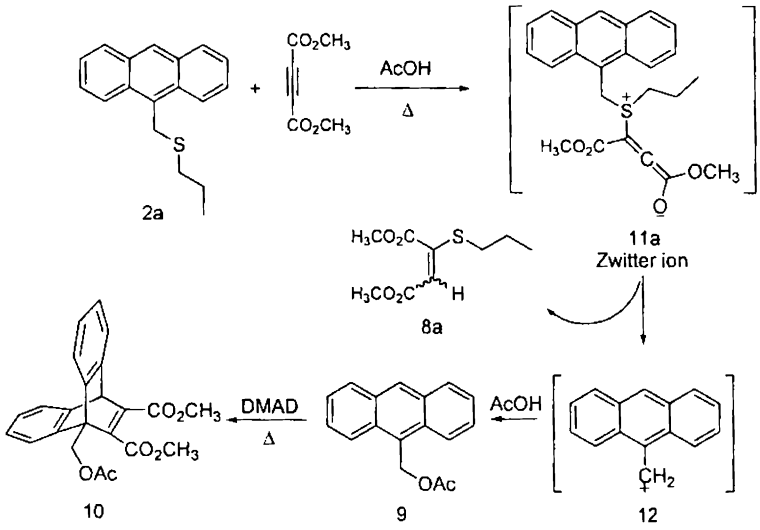
The mechanism of the reaction was confirmed through GC-MS analysis of the reaction mixture. Absence of dimethyl-(2-propanethio)-maleate/fumarate in the product mixture rules out the possibility of an ionic mechanism (*vide infra*). As with the reactions of amines, the sulphane component formed through the C-S bond cleavage of the radical ion pair may be a low volatile component which is likely to be lost through the course of

the reaction or during the reaction workup. We could not detect any such products from the GC-MS analysis of the reaction mixture either.

We conclude that under non-polar reaction conditions, (anthracen-9-yl)methylsulphanes undergo electron transfer reactions as well as cycloaddition reactions with DMAD. An electron-transfer mediated C-S bond cleavage followed by dimerisation and intramolecular Diels-Alder reaction lead to the formation of lepidopterene. Like (anthracen-9-yl)methylamines, (anthracen-9-yl)methylsulphanes also give electron transfer reactions with reactive dienophiles like DMAD under non-polar reaction conditions but in addition, cycloaddition reactions are also feasible in the latter case leading to Diels-Alder adducts in good yields.

5.3.2.2. Reactions in Polar Solvents.

We conducted the reaction of (anthracen-9-yl)methylsulphane **2a** with DMAD in glacial acetic acid under reflux for 2 hours. Unlike the reactions of amines, we observed the formation of dimethyl (2-propanethio)maleate/ fumarate[26] (**8a**) in the reaction along with (anthracen-9-yl)methyl acetate and the corresponding barrelene derived thereof (Scheme 4). Formation of **8a** under these conditions indicates nucleophilic addition of sulphane to DMAD giving rise to a Michael-type adduct **11**, which undergo a C-S bong cleavage generating 9-anthracenemethyl cation (**12**) and dimethyl (2-propanethio)maleate/fumarate (**8a**) (Scheme 5).



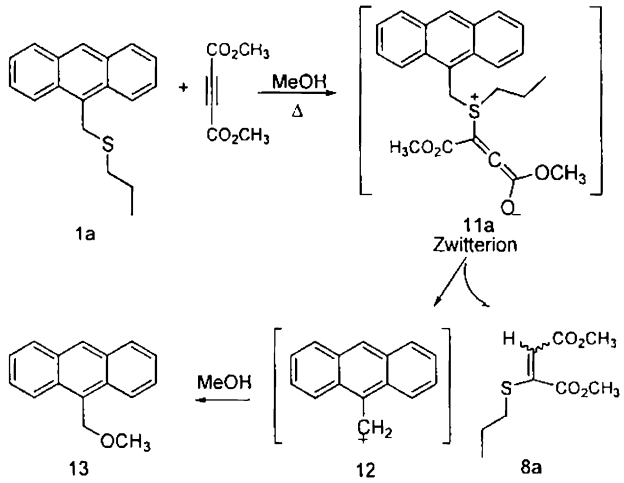
Scheme 4

The results presented in Scheme 4 points to very interesting observations on the reactivity of (anthracen-9-yl)methylsulphanes. Expected Diels-Alder adduct **5a** was not detected in the reaction mixture. This observation should be assessed in the context of the formation of **10** through Diels-Alder reaction of **9** with DMAD. So, it is clear that the reaction conditions selected by us are suitable for successful Diels-Alder reaction between anthracenes and DMAD. Though both **2a** and **9** are equally disposed to undergo Diels-Alder reactions, the absence of **5a** in the reaction mixture indicates exclusive nucleophilic addition reaction of (anthracen-9-yl)methylsulphane to DMAD in acetic acid solvent. Based on these observations, we conclude that, for sulphane **2a**, Diels-Alder reactions is not competitive with nucleophilic addition pathway under the conditions applied by us.

Though the overall reaction of **2a** with DMAD in acetic acid resembles those of (anthracen-9-yl)methylamines with DMAD in acetic acid, a few subtle differences are worth mentioning. Unlike with amines where electron transfer mediated nucleophilic substitutions predominated, Michael-type

addition followed by C-S bond cleavage leading to 9-anthracenemethyl cation and dimethyl (2-propanethio)maleate/fumarate (**8a**) is the major reaction pathway followed by sulphanes. Based on available results, we had concluded that single electron transfer followed by C-N bond cleavage leading to 9-anthracenemethyl cation and aminium radical is more likely with (anthracen-9-yl)methylamines.

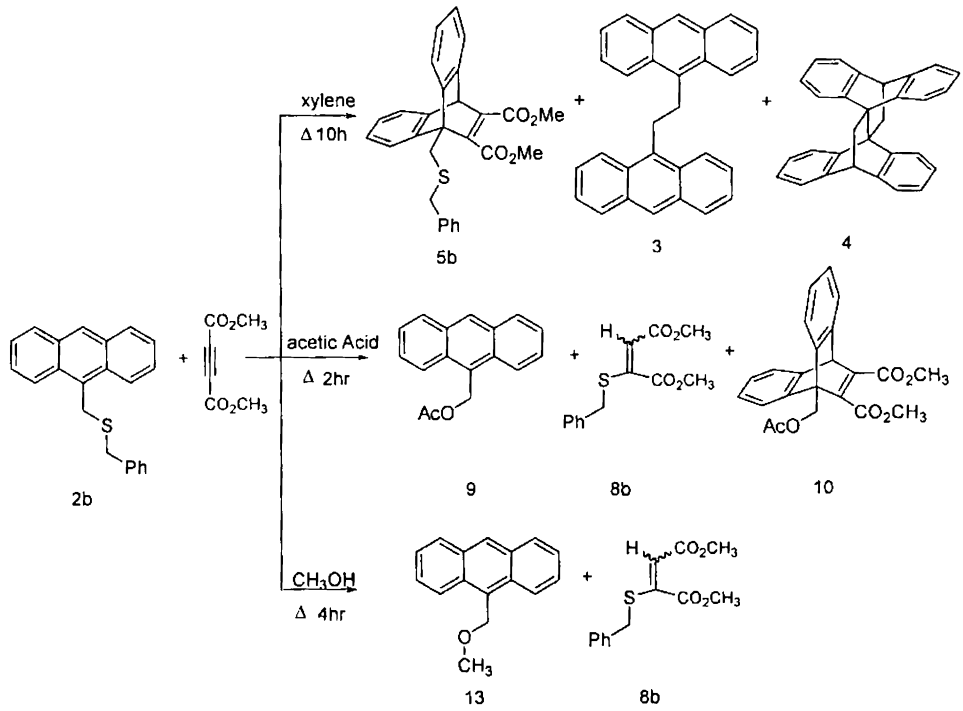
In continuation, we carried out the reaction of (anthracen-9-yl)methylsulphane **2a** with DMAD in methanol under reflux for 4 hours. As with anthracenemethanamines, we observed the formation of 9-(methoxymethyl)anthracene (**13**) along with dimethyl (2-propanethio)maleate/fumarate (**8a**) (Scheme 5). The reaction takes place through a Michael-type addition of sulphane to DMAD leading to the formation of **11a**. A heterolytic C-S bond cleavage in **11a** generates 9-anthracenemethyl cation (**9**) and dimethyl (2-propanethio)maleate/fumarate (**8a**) (Scheme 5). Since the reaction was carried out in a low boiling solvent such as methanol, no Diels-Alder adducts were formed in this case.



Scheme 7

Hence the reaction of (anthracen-9-yl)methylsulphanes in polar solvents take place through a Michael-type addition mechanism leading to the formation of a zwitterion **11**, followed by a C-S bond heterolysis to give 9-anthracenemethyl cation. The cation formed reacts with the solvents to give the substituted products.

Similar results were obtained when we carried out the reaction using **2b**. The ^{1}HNMR spectrum of the reaction mixture carried out in nonpolar solvents indicated the presence of the Diels-Alder adduct **5b** along with **3** and **4**. For the reaction in acetic acid and methanol solvents, we observed the formation of **8b** along with other products that confirmed the nucleophilic addition mechanism operating here as in the case of **2a** (Scheme 8).



Scheme 8

The difference in reactivity of (anthracen-9yl)methylamines and (anthracen-9-yl)methylsulphanes may be due to difference in the steric and electronic environment of the donor site. (Anthracen-9-yl)methylsulphanes, with only two substituent groups around the significant atom (sulphur, in this case) suffer less steric hindrance in comparison with the analogous amines having three substituents on the significant atom (nitrogen, in this case). Moreover, sulphanes are better nucleophiles than amines. These factors increase the possibility of closer and more productive encounter between sulphanes and DMAD favouring cycloaddition along with Michael-type addition reactions. Hence the reactions take place at much faster rates in the case of (anthracen-9-yl)methylsulphanes than with (anthracen-9-yl)methylamines.

5.4. Conclusion

In summary, we have illustrated solvent dependant reaction of (anthracen-9-yl)methylsulphanes with a reactive dienophile like DMAD. Under nonpolar reaction conditions, both cycloaddition and electron transfer reactions are favoured for (anthracen-9-yl)methylsulphanes whereas for (anthracen-9yl)methylamines electron transfer reactions predominates over cycloaddition in their reactions with reactive acetylenes. Both these pathways take place more efficiently in (anthracen-9-yl)methylsulphanes than with analogues (anthracen-9-yl)methylamines. In the case of (anthracen-9-yl)methylamines electron transfer mediated nucleophilic substitution takes place in acetic acid solvent and a completely ionic mechanism leading to a Michael-type adduct is followed in alcohol solvents. On the other hand, in their reaction with DMAD in both acetic acid and methanol, (anthracen-9-yl)methylsulphanes follow Michael type addition pathway leading to a

completely ionic reaction generating 9-anthracenemethyl cation and the products derived thereof.

Thus we have illustrated solvent dependent reactions of (anthracen-9-yl)methylsulphanes with DMAD and the results indicate that sulphanes behave somewhat analogously with amines in their reactions with reactive dienophiles like DMAD. The efficiency of these reactions paves way for successful nucleophilic substitution reactions on systems where classical nucleophilic substitution is not favoured due to the absence of good nucleofuges. Ground state electron transfer reactions of (anthracen-9-yl)methylamines and (anthracen-9-yl)methylsulphanes illustrated by us are novel *vis-à-vis* the observations reported so far.

5.5. Experimental

5.5.1. General Procedures

All melting points are uncorrected and were determined on a Neolab melting point apparatus. All reactions and chromatographic separations were monitored by thin layer chromatography (TLC). Glass plates coated with dried and activated silica gel or aluminium sheets coated with silica gel (Merck) were used for thin layer chromatography. Visualisation was achieved by exposure to iodine vapours or UV radiation. Column chromatography was carried out with slurry-packed silica gel (Qualigens, 60-120 mesh). Absorption spectra were recorded using Shimadzu 160A spectrometer and infra red spectra were recorded using ABB Bomem (MB Series) FT-IR spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded at 300, 400 and 500 MHz on a Bruker FT-NMR spectrometers with tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in parts per million (ppm) downfield of TMS. Elemental analysis was performed using Elementar Systeme (Vario ELIII) and GC-MS analysis was carried out using Varian 2000 L Single Quadrupole instrument. We have reported only the relevant data for the characterisation of novel compounds synthesised by us.

5.5.2. Starting Materials. All standard reagents were purchased from S. D. Fine Chem. Ltd. and were used as obtained. Dimethyl acetylenedicarboxylate (DMAD) was purchased from Sigma-Aldrich and was used as obtained. Solvents were distilled and dried as per requirements.

5.5.2.1. 9-Chloromethylanthracene: 9-Chloromethylanthracene was prepared by a known method[27] (84%, mp 136-138 ^{0}C).

5.5.3. Preparation of (Anthracen-9-yl)methylsulphanes

5.5.3.1. Preparation of ((Anthracen-9-yl)methyl)(propyl)sulphane (2a).

To a solution of 9-chloromethylanthracene (2.50 g, 11 mmol) in 10 mL of dry benzene, propanethiol (1.70g, 14 mmol) and triethylamine were added and the mixture was stirred at RT for 24 h. The reaction mixture was poured into water and extracted with diethyl ether. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. The ether layer was evaporated and the solid obtained was passed through a silica column. Elution with a mixture (3:1) of hexane and dichloromethane gave **2a** (2.3 g). The solid obtained upon removal of solvent was purified by recrystallisation from a mixture (1:3) of hexane and dichloromethane.

Compound 2a: (78%); mp 92-94 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$), δ 1.00 (3H, t, J = 7.3 Hz), 1.70-1.82 (2H, m), 2.8 (2H, t, J =7.3 Hz), 4.75 (2H, s), 7.46-8.41 (9H, m, aromatic); ^{13}C NMR (100 MHz, $CDCl_3$) δ 53.70, 54.59, 67.15, 124.89, 125.03, 125.69, 127.62, 129.01, 131.40, 131.44; MS, *m/z* 266 (M^+), and other peaks. Anal. Calcd for $C_{18}H_{18}S$: C, 81.15; H, 6.81; S, 12.04. Found: C, 81.19; H, 6.78; S, 12.03.

5.5.3.2. Preparation of ((Anthracen-9-yl)methyl)(benzyl)sulphane (2b).

To a solution of 9-chloromethylanthracene (2.50g, 11 mmol) in 10 mL of dry benzene, benzylthiol (1.71g, 14 mmol) and DBU (1.25 eq.) were added and the mixture was stirred at RT for 24 h. The reaction mixture was poured into water and extracted with diethyl ether. The organic layer was separated, washed with water, and dried over anhydrous Na_2SO_4. The ether layer was evaporated and the solid obtained was passed through a silica column. Elution with a mixture (2:1) of hexane and dichloromethane gave **2b** (1.91g). The

solid obtained upon removal of solvent was purified by recrystallisation from a mixture (1:2) of hexane and dichloromethane.

Compound 2b: (55%); mp 103-105 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (2H, s), 4.56 (2H, s), 7.29-8.34 (9H, m, aromatic); ^{13}C NMR (400 MHz, $CDCl_3$) δ 53.70, 54.59, 67.15, 124.89, 125.03, 125.69, 127.62, 129.01, 131.40, 131.44; MS, *m/z* 314 (M^+), and other peaks. Anal. Calcd for $C_{22}H_{18}S$: C, 84.03; H, 5.77; S, 10.20. Found: C, 84.12; H, 5.65; S, 10.23.

5.4.4. Reaction of (Anthracen-9-yl)methylsulphanes with DMAD in Xylene.

5.5.4.1. Reaction of ((Anthracen-9-yl)methyl)(propyl)sulphane (2a).

To a solution of **2a** (2.2 g, 8 mmol) in dry toluene (15 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed under nitrogen atmosphere for 48 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:6) of hexane and dichloromethane gave **3** (traces). Further elution with a mixture (1:7) of hexane and dichloromethane gave lepidopterene (**4**) (0.54 g, 35%). Further elution with dichloromethane gave **5a** (1.37 g, 42%). The products were characterized by NMR and crystal studies.

Compound 3: (traces); mp 310-314[28] ^{0}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.07 (4H, s), 7.45-8.42 (18H, m, aromatic); Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80; Found: C, 94.22; H, 5.79.

Compound 4: (35%); mp 316-318 ^{0}C[29]; IR ν_{max} (KBr) 1460 cm^{-1}, 2950 cm^{-1}, 2990 cm^{-1}, 3020 cm^{-1}, 3080 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.90 (4H, d, *J* = 3.0 Hz), 4.63 (2H, t, *J* = 3.0 Hz), 6.71-7.34 (16H, m, aromatic); ^{13}C NMR (300 MHz, $CDCl_3$) δ 28.93, 45.58, 54.01, 122.22, 122.35, 122.64, 125.48,

143.15, 143.40; Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.80; Found: C, 94.29; H, 5.82.

Compound 5a: (42%); mp 138-142 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.10 (3H, t, *J* = 7.3 Hz), 1.78 (2H, m), 2.72 (2H, t, *J* = 7.3 Hz), 3.39 (2H, s), 3.72 (3H, s), 3.75 (3H, s), 5.55 (1H, s), 6.96-7.51 (8H, m, aromatic); Anal. Calcd for $C_{30}H_{22}$: C, 70.56; H, 5.92; S, 7.85; Found: C, 70.51; H, 5.88; S, 7.83.

5.5.4.2. Reaction of ((Anthracen-9-yl)methyl)(benzyl)sulphane (2b).

To a solution of **2b** (2.51 g, 8.00 mmol), in dry toluene (15 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed under nitrogen atmosphere for 48 h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Elution with a mixture (1:6) of hexane and dichloromethane gave **3** (traces). Further elution with a mixture (1:7) of hexane and dichloromethane gave lepidopterene (**4**) (380 mg, 22%). Further elusion with dichloromethane gave **5b** (910 mg, 25%).

Compound 3: (traces); mp 310-314 ^{0}C

Compound 4: (22%); mp 316-318 ^{0}C

Compound 5b: (25%); mp (mixture) 121-126 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.75(3H, s), 3.73 (3H, s), 3.86 (2H, s), 3.80(2H, s), 6.91-7.52 (13H, m, aromatic); Anal. Calcd for $C_{30}H_{22}$: C, 73.66; H, 5.30; S, 7.02; Found: C, 73.58; H, 5.29; S, 7.13.

5.5.5. Reactions (Anthracen-9-yl)methylsulphanes with DMAD in Acetic Acid.

5.5.5.1. Reaction of ((Anthracen-9-yl)methyl)(propyl)sulphane (2a).

To a solution of **2a** (2.18 g, 8.00 mmol) in glacial acetic acid (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed for 2 h. Solvent was removed under reduced pressure and the residue was washed with a 5% solution of sodium bicarbonate and extracted with dichloromethane. The organic extracts were combined and dried over $MgSO_4$ and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution of the column with a mixture (1:8) of hexane and dichloromethane gave compound **9** (900 mg, 35%). Further elution with a mixture (1:9) of hexane and dichloromethane gave compound **10** (850 mg, 27%). Further elution with dichloromethane gave **8a** (780 mg, 45%).

Compound 8a: (45%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (3H, t, J = 10 Hz), 1.70-1.82 (2H, m), 2.65 (2H, t, J = 10 Hz), 3.57(3H, s), 3.87 (3H, s), 5.69 (1H, s); GC-MS, *m/z* 218 (M^+) and other peaks; Anal. Calcd for $C_9H_{14}O_4S$: C, 49.52; H, 6.47; S, 14.69; Found: C, 49.49; H, 6.55; S, 14.61.

Compound 9: (45%); mp 108-110 ^{0}C; IR ν_{max} (KBr) 1249 cm^{-1}, 1726 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.09 (3H, s); 6.16 (2H, s), 8.05-7.47 (9H, m, aromatic), ^{13}C NMR (300 MHz, $CDCl_3$) δ 21.01, 58.82, 123.94, 125.16, 126.26, 126.75, 129.12, 129.27, 131.18, 131.43, 171.39; GC-MS, *m/z* 250 (M^+), 191 (base peak) and other peaks; Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64; Found: C, 81.51; H, 5.58.

Compound 10: (27%); mp 161-163 ^{0}C ; IR ν_{max} (KBr) 1231 cm^{-1}, 1715 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.13 (3H, s), 3.75 (3H, s), 3.76 (3H, s), 5.44

(2H, s), 5.62 (1H, s), 7.41-7.03 (8H, m, aromatic); GC-MS, *m/z* 392 (M^+) and other peaks; Anal. Calcd for $C_{23}H_{20}O_6$: C, 70.40; H, 5.14; Found C, 70.38; H, 5.20.

5.5.5.2. Reaction of ((Anthracen-9-yl)methyl)(benzyl)sulphane (2b).

To a solution of **2b** (2.51 g, 8 mmol) in glacial acetic acid (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed for 2 h. Solvent was removed under reduced pressure and the residue was washed with a 5% solution of sodium bicarbonate and extracted with dichloromethane. The organic extracts were combined and dried over $MgSO_4$ and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel using a mixture (1:8) of hexane and dichloromethane gave compound **9** (700 mg, 35%) and elution with a mixture (1:9) of hexane and dichloromethane gave compound **10** (560 mg, 18%). Further elution with dichloromethane gave **8b** (740 mg, 35%).

Compound 8b: (35%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.89 (3H, s), 3.61(3H, s), 3.82 (2H, s), 5.91 (1H, s), 7.40-7.24 (5H, m, aromatic); GC-MS, *m/z* 266 (M^+) and other peaks; Anal. Calcd for $C_{13}H_{14}O_4S$: C, 58.63; H, 5.30; S, 12.04; Found: C, 58.69; H, 5.36; S, 12.11.

Compound 9: (35%); mp 109-111 ^{0}C

Compound 10: (18%); mp 161-163 ^{0}C

5.4.6. Reactions ((Anthracen-9-yl)methylsulphanes with DMAD in Methanol.

5.5.6.1. Reaction of ((Anthracen-9-yl)methyl)(propyl)sulphane (2a).

To a solution of **2a** (1.76 g, 8 mmol) in methanol (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed for 4 h. Solvent was removed

under reduced pressure and the residue obtained was purified by column chromatography on silica gel. Elution with a mixture (1:5) of hexane and dichloromethane gave compound **13** (1.17 g, 66%). Further elution with dichloromethane gave compound **8a** (1.04 g, 60%).

Compound 13: (66%); mp 88-90 ^{0}C; IR ν_{max} (KBr) 1185 cm^{-1}, ^{1}H NMR (400 MHz,$CDCl_3$) δ 3.53 (3H, s), 5.42 (2H, s), 8.45-7.44 (9H, m, aromatic protons); ^{13}C NMR (400 MHz, $CDCl_3$) δ 58.42, 66.59, 124.32, 125.11, 126.26, 128.50, 129.02, 121.07, 131.58, 134.03; GC-MS, *m/z* 222 *(M^+)* and other peaks; Anal. Calcd for $C_{16}H_{14}O$: C, 86.45; H, 6.35; Found: C, 86.38; H, 6.31.

Compound 8a: (60%); GC-MS, *m/z* 218 *(M^+)*

5.5.6.2. Reaction of ((Anthracen-9-yl)methyl)(benzyl)sulphane (2b).

To a solution of **2b** (2.51 g, 8 mmol) in methanol (10 mL), DMAD (2.00 g, 14 mmol) was added and the mixture was refluxed for 4 h. Solvent was removed under reduced pressure and the residue obtained was purified by column chromatography on silica gel. Elution of the column with a mixture (1:5) of hexane and dichloromethane gave compound **13** (780 mg, 45%). Further elution with dichloromethane gave **8b** (850 mg, 40%).

Compound 8b: (40%); GC-MS, *m/z* 266 *(M^+)*

Compound 13: (45%); mp 88-91 ^{0}C; GC-MS, *m/z* 222 *(M^+)* and other peaks.

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