GROUND AND EXCITED STATE ELECTRON TRANSFER REACTION BETWEEN A FEW ANTHRACENE APPENDED TERTIARY AMINES AND SUITABLE ELECTRON ACCEPTORS

Thesis submitted to the
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in

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by

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under the supervision of

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January 2013

DECLARATION

I hereby declare that the work presented in the thesis entitled "Ground and Excited State Electron Transfer Reaction Between a few Anthracene Appended Tertiary Amines and Suitable Electron Acceptors" is my own unaided work under the supervision of Dr. Prathapan S., Associate Professor of Organic Chemistry, Department of Applied Chemistry, Cochin University of Science and Technology, Cochin-22, and the same has not been submitted elsewhere for the award of any other degree.

Cochin-22 Jomon P. Jacob

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CERTIFICATE

This is to certify that the thesis entitled "Ground and Excited State Electron Transfer Reaction Between a few Anthracene Appended Tertiary Amines and Suitable Electron Acceptors" is a genuine record of research work carried out by Mr.Jomon P. Jacob, 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 the award of any other degree.

Cochin-22
30-01-2013

Dr.Prathapan S.
(Supervising Guide)

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Jomon P. Jacob

PREFACE

Electron transfer reactions play a major role in electrochemical, photochemical and biochemical redox processes. Electron transfer reaction is the process of moving electrons from one atom to another. Electron transfer reactions of amines are very important because the lone pair of electrons on the nitrogen atom is very easy to oxidize.

Amines undergo single electron transfer reactions under thermal and photochemical conditions and two electron transfer reactions like electrophilic, nucleophilic substitution and addition reactions. Amine radical cations are major intermediates in one electron transfer reactions. Michael addition reaction is a well-known example for two electron transfer reaction. Diels-Alder reaction is one of the most useful reactions for the formation of carbon-carbon bonds in synthetic organic chemistry. Anthracene and its derivatives very easily undergo both thermal and photochemical Diels-Alder addition with a variety of dienophiles across 9 and 10 positions.

Upon excitation, amines undergo electron transfer reaction to form amine radical cations followed by secondary reactions to yield α-aminoalkyl radical, which provides a useful pathway for the synthesis of carbon-carbon bond and many alkaloid derivatives.

In order for electron transfer reactions to proceed smoothly, suitable one or two electron donors and acceptors should be available in the substrates. Incorporation of reactive diene

component will enable amines to undergo Diels-Alder reactions as well. These reactions also depend on the nature of solvents, concentration and temperature.

Our aim is to study one electron transfer, two electron transfer and Diels-Alder reactions in a single system. So we have selected (anthracen-9-yl)methanamines, having 'donor-spacer-acceptor' geometry. Here the spacer helps to shut the direct electronic communication between anthracene and amine moiety, thereby undergo the above three types of electron transfer reactions easily in the presence of suitable electron acceptors. These photoactive substrates also show photoinduced electron transfer reactions.

In this situation, the thesis entitled "***Ground and Excited State Electron Transfer Reaction Between a few Anthracene Appended Tertiary Amines and Suitable Electron Acceptors***" portrays our attempts to explore the solvent, concentration and temperature effect of the reaction between a few (anthracen-9-yl)methanamines with electron acceptors like DMAD, DBA and DBE. We have also studied the effect of solvent and percentage fluorescence quenching in the photoinduced electron transfer reactions of these 'donor-spacer-acceptor' systems. Finally we look in to the intramolecular electron transfer reactions of a few tertiary amine appended dibenzobarrelenes and bisdibenzobarrelenes.

The thesis is organized in to five chapters. The first chapter briefly introduces Michael addition reactions, Diels-Alder reactions

and both thermal and photoinduced electron transfer reactions of amines. The research problem is defined at the end of this chapter. The second chapter describes the synthesis of a few (anthracen-9-yl)methanamines. Results of our investigations on the solvent, concentration and temperature dependency of the reactions of (anthracen-9-yl)methanamines with suitable electron acceptors are presented in the third chapter. Fourth chapter gives an idea about the effect of solvent and fluorescence quenching on photoinduced electron transfer reaction of (anthracen-9-yl)methanamines. Results of the photochemical transformations of a few tertiary amine appended dibenzobarrelenes and bisdibenzobarrelenes are described in chapter five.

Each chapter of the thesis is as an independent unit and therefore the structural formulae, schemes and figures are numbered chapterwise. All new compounds are fully characterized on the basis of their spectral and analytical data. Relevant data for the characterization of novel compounds synthesised by us are reported. A comprehensive list of references is included at the end of each chapter.

List of Abbreviations

AcOH	: acetic acid
ATP	: adenosine triphosphate
br	: broad
br s	: broad singlet
CAN	: ceric ammonium nitrate
CTAN	: ceric tetrabutylammonium nitrate
DBA	: dibenzoylacetylene
DBE	: dibenzoylethylene
DCM	: dichloromethane
DCA	: dicyanoanthracene
DCN	: dicyanonaphthalene
DMAD	: dimethyl acetylenedicarboxylate
DMF	: dimethylformamide
d	: doublet
dd	: doublet of doublet
E	: entgegen
EtOH	: ethanol
HOMO	: highest occupied molecular orbital
LUMO	: lowest unoccupied molecular orbital
mg	: milligram
mL	: millilitre
NMR	: nuclear magnetic resonance
ORTEP	: Oak Ridge Thermal Ellipsoid Plot Program
PET	: photoinduced electron transfer
quin	: quintet
RT	: room temperature
s	: singlet
SET	: single electron transfer
SOMO	: singly occupied molecular orbital
t	: triplet
Z	: zusammen

CONTENTS

CHAPTER 1

ELECTRON TRANSFER REACTIONS OF AMINES - A BRIEF DISCUSSION

1.1. Abstract

This chapter gives a general idea on electron transfer processes in biological and chemical reactions. Here we have described both one and two electron transfer reactions of amines and Diels-Alder reactions. We have also briefly explained the photoinduced electron transfer reactions of amines.

1.2. Electron Transfer Reactions – General Survey

Electron transfer reactions involve the process of moving electrons from one atomic or molecular unit to another. By definition, it means change in electronic configuration of the reacting species.[1] This reaction accompanied by proton and hydrogen atom transfer occurs in many biological processes like photosynthesis, nitrogen cycle, cellular respiration etc. In the biological systems, electron transfer occurs in series in an organized assembly of proteins. These proteins have metal ions

capable of existing in different oxidation states. The metal ions are embedded in the ligand system that responds to change in the oxidation states, thereby facilitating the relocation of electron from one part to another. Porphyrins, the tetrapyrrole macrocycles (Figure **1.1**) are important ligands which enable the transfer of electrons that are finally captured by biological acceptor molecules. There is a parallel movement of protons in the vicinity of the system corresponding to electron transfer to maintain the electrical neutrality so as to avoid the accumulation of charges.[2]

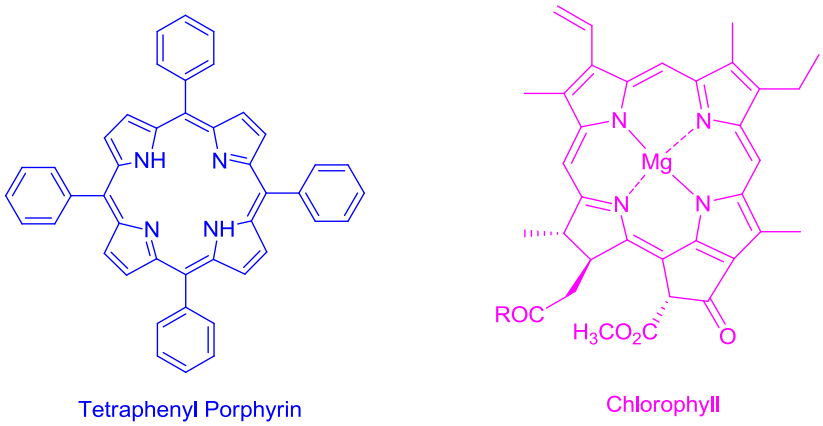


Figure 1.1

Energy required for cell existence, growth and all other functions of higher organisms is obtained by the oxidation of glucose.[3] The molecule which serves the energy for above processes is adenosine triphosphate (ATP) through a series of controlled oxidation-reduction reactions. The metabolic pathway for the production of ATP was classified into fermentive and oxidative. Oxidation of one molecule of glucose to CO_2 and water

by the combination of glycolysis (fermentive pathway) and the tricarboxylic acid cycle (oxidative pathway) yields two ATPs and thirty six ATPs respectively.[4,5](Figure **1.2**).

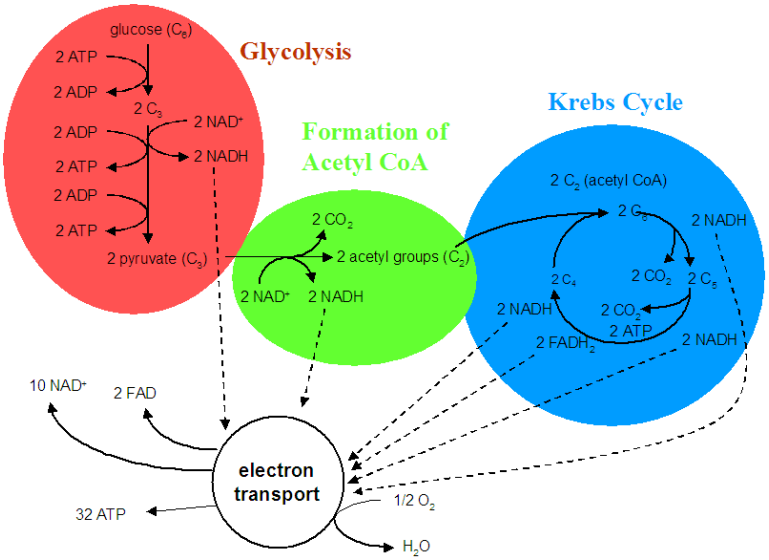


Figure 1.2

Plants and animals cannot use N_2 gas directly, so it must be converted into a usable form. This transformation can be carried out through both biological and physical processes. Important steps in the nitrogen cycle are fixation, mineralization, nitrification and dentrification. Conversion of atmospheric nitrogen to ammonia achieved by microorganisms is called nitrogen fixation. Here two moles of ammonia are produced from one mole of nitrogen at the expense of sixteen moles of ATP and by the supply of electrons and protons. From the dead organisms, organic nitrogen is converted into ammonium ion which is known as ammonification

or mineralization. The process of conversion of ammonium ion to nitrate by soil-living bacteria is called nitrification. Dentrification is the reduction of nitrate to N_2 gas, completing the nitrogen cycle by microorganisms. So in the nitrogen cycle, nitrogen can be found in different oxidation states, from +5 in the nitrate to -3 in the ammonium ion.[6]

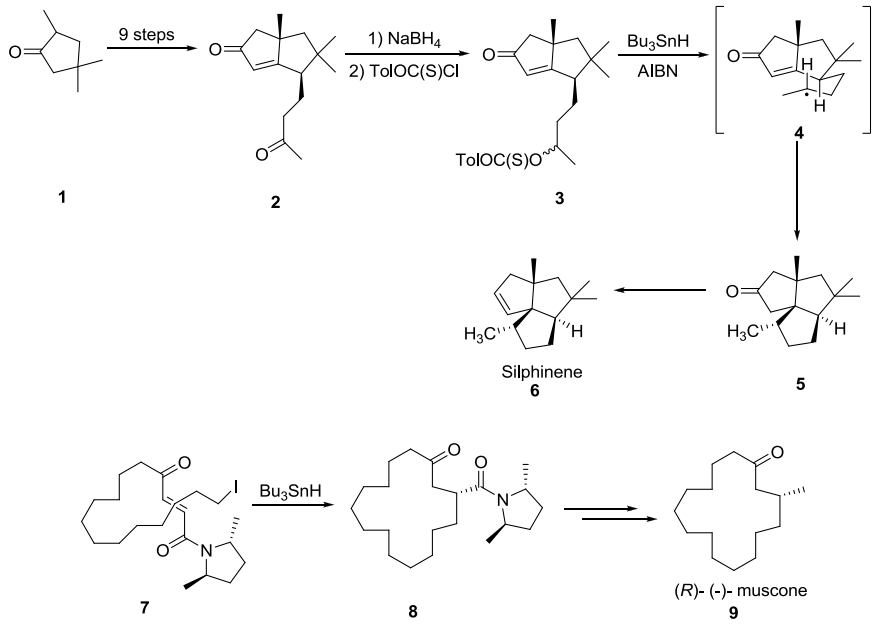
As in the case of biological reactions, electron transfer is also a central process in chemical reactions. Chemical transformations initiated by injection or removal of electrons from organic molecules attracted much attention over the last four decades. Electrons are not bound equally in all atoms, some of them have tightly bound electrons than others. Electron rich systems which readily give electrons are termed as donors and electron deficient systems which generally pick up electrons are referred to as acceptors. According to Marcus, electron transfer occurs only if there is a suitable electronic coupling between the reacting species and if there is a suitable fluctuation of coordinates like bond distance, orientation of solvent molecule and position of ions in atmosphere of both reactants and products.[7] Electron transfer not only changes the distribution of the electron density but also self-energy of the electronic sub system of the donor-acceptor complex. This change in self-energy arises from the difference in polarization of the electronic cloud of the donor-acceptor complex by the solvent in the reactant and product states.[1]

Free radicals are highly versatile and reactive intermediates which are involved in many chemical and biological reactions.

Reactive radical ions are generated by electrochemical reaction, photochemical reaction or by the reaction of redox reagents using thermal excitation energy. Electron loss from a diamagnetic organic molecule results in the formation of a radical cation and electron gain results in radical anion formation. This causes large change in bond strength, initiating bond cleavage or addition reactions.[8] Electrophilic and nucleophilic reactions come under electron transfer reactions. Both aliphatic and aromatic substrates undergo nucleophilic substitution reactions. In aliphatic family, SN1, SN2 and related two electron transfer reactions predominate. But in aromatic family, two electron processes like SNAr, benzyne and halogen-metal exchange mechanism usually account for nucleophilic substitution reaction. Nucleophilic substitution and addition reactions depend on the substrate, nucleophile and the reaction condition. Generally these reactions are two electron transfer processes and their mechanism depends up on the above factors.

Homolytic cleavage of bonds leads to the formation of radicals. Use of radicals in organic synthesis has been increased dramatically in the last few decades.[9] This is due to the fact that radical reactions have many advantages. Carbon-centered radicals, for example, are highly reactive but inert towards -OH or -NR_2 groups. So radical reactions do not need dry condition and are immune to presence of hydroxyl and amine functionalities. In contrast to carbocations, radicals neither catch alkoxy or tertiary amino group nor eliminate β-hydrogen. Tributyltin hydride is

mainly used to conduct free radical reactions. In the synthesis of natural products having six membered ring, tributyltin hydride was first used in radical cyclization reaction. Tributyltin hydride was also used in the synthesis of natural products having five membered and large rings[10] (Scheme **1.1**).



Scheme 1.1

Amines generally show electron transfer like radical reactions in thermal and photochemical conditions, electrophilic and nucleophilic substitution-addition reactions than any other functional groups. Electron transfer reactions of different types of amines under different conditions form the subject matter of this thesis. In this chapter, we introduce different types of electron transfer reactions that are shown by amines.[11]

1.3. Electron Transfer Reactions of Amines

In nature, amines and their derivatives are more widely distributed than any other functional group family. Electron transfer reactions of amines are very important because the lone pair of electrons on nitrogen atom is very easy to oxidize. Hence amines are used in several electrochemical,[12-14] photochemical[15-23] and biochemical redox processes.[24-27] Radical intermediates are formed by one electron oxidation of amines, that can be used for the synthesis of alkaloids, amino acids and several other nitrogen-containing compounds of biological and pharmaceutical importance.[28-32]

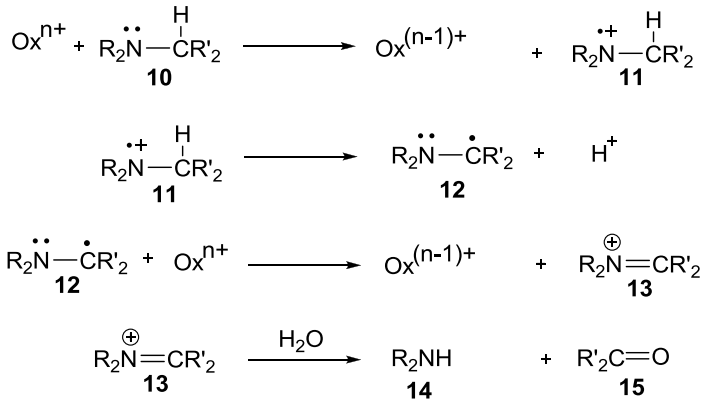
The core process in several technological applications such as imaging,[33] photopolymerisation[34,35] and fading of textile dyes[36] are electron transfer reactions of amines. Electron donating capacity of amine functionality has been extensively used for designing new materials such as fluoroionophores,[37,38] organic conductors,[39] electroluminescent materials,[40-42] photovoltaics,[43,44] and materials with nonlinear optical activity.[45,46] Thermochemical, electrochemical, photochemical and radiation chemical techniques are used for studying the mechanism of electron transfer reactions of amines.

1.3.1. Thermal Oxidation of Amines and its Synthetic Applications

A variety of chemical oxidants are initiated by electron transfer reactions of amines. The products are formed by one electron oxidation of amines, when amines react with metal salts such as ceric ammonium nitrate (CAN),[30,47-49] manganese oxalate,[30] alkaline ferricyanide,[50-53] phenanthroline complexes of iron[52] and octacyanomolybdate.[53] Mechanisms of electron transfer catalysed reactions of amines by chlorine dioxide[53,54] and permanganate[55] have been intensively investigated in aqueous solutions. *N*-bromosuccinimide in carbontetrachloride[56] and *N*-chlorobenzotriazole in benzene[57] were reported to react with amines via single-electron transfer (SET) in nonaqueous solvents. Oxidation reactions of vinyl amines with molecular oxygen[58,59] and of aromatic amines with nitrogen dioxide[60] catalysed by metal ions have been reported. Hydrogen peroxide and peracids react with amines in the presence of transition metal ions liberating hydroxyl radicals[61-65] either via electron transfer or hydrogen atom transfer. It has been proposed that oxidation of amines catalysed by enzymes such as amine oxidases[27] and cytochrome P-450[24] occurs *via* SET processes. Amine oxides or hydroxylamines are usually formed by two-electron oxidation of amines with reagents like hydrogen peroxide, peroxy acid or ozone.[31]

Chlorine dioxide or ferricyanide is used as the oxidant for studying the mechanism of amine oxidation because 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. Proposed mechanism for electron transfer based on these investigations is presented in Scheme **1.2**.

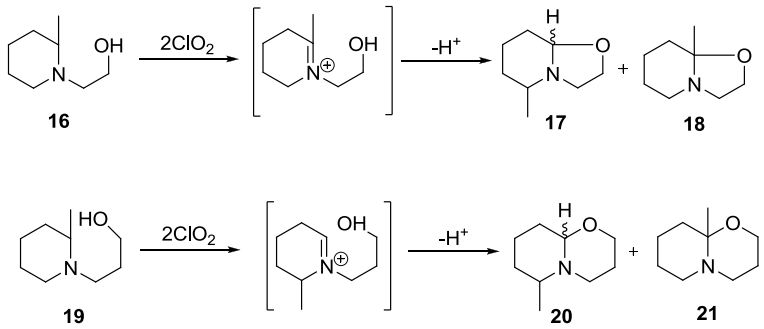


Scheme 1.2

The amine radical cation **11** formed by the initial one electron transfer process of amines **10** undergoes deprotonation at the α-carbon to form amino alkyl radical **12**. The amino alkyl radical undergoes further oxidation to yield the iminium salt **13** which hydrolyses to the dealkylated amine **14** and a carbonyl compound **15**. 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.[66] Permanganate on the other hand reacts with

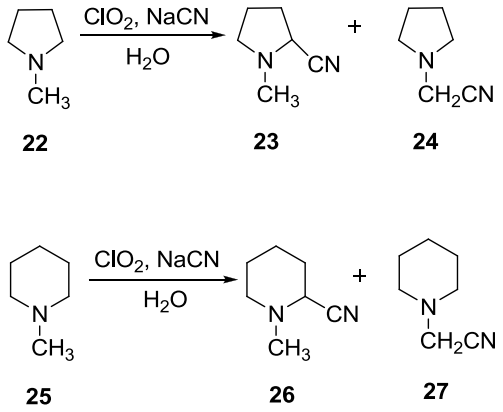
triethylamine exclusively by electron transfer,[55] whereas it reacts with benzylamines predominantly via hydrogen atom abstraction.[67] Formation of imines,[68,69] benzonitrile,[70] diazines,[71] anilines,[72] and *N*-benzylidinebenzylamines[69,70,72] apart from dealkylated amine and benzaldehyde[70,71,73] by the oxidation of benzylamines has also been observed.

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.[11] Thermal, electrochemical and photochemical methods are used for initiating amine oxidation reactions. Because of the relative instability of amine radicals, their synthetic applications in thermal one-electron-catalysed reactions are rare. Metal catalysed degradation of chloramines and hydroxylamines leads to the formation aminium radicals which can undergo a variety of synthetically useful reactions such as inter and intramolecular addition of olefins and in aromatic amination reactions. Chlorine dioxide was used to generate and trap iminium ions *in situ* using both internal and external nucleophiles yielding a variety of nitrogen heterocycles and α-substituted amines. Chlorine dioxide catalysed cyclisation of tertiary aminoalcohols **16** and **19** to oxazolidines **17** and **18** and tetrahydro-1,3-oxazines **20** and 2**1** in basic aqueous medium has been reported[74] (Scheme **1.3**).



Scheme 1.3

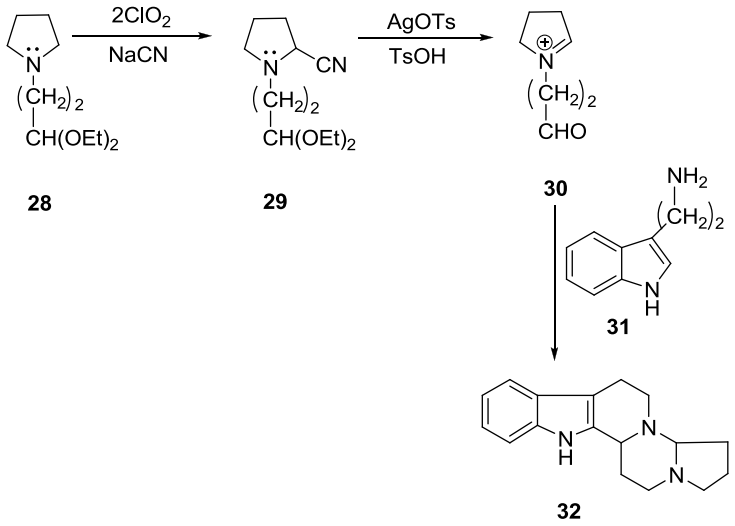
Chlorine dioxide on reaction with tertiary amines in the presence of 5-7 equivalents of aqueous sodium cyanide as an external nucleophile gives α-cyano substituted tertiary amines[74] (Scheme **1.4**). Thus, aqueous chlorine dioxide can be used as a potentially useful alternative to $Hg(OAc)_2$ oxidation (*vide infra*).



Scheme 1.4

Advantage of chemoselectivity of ClO_2 based oxidative cyanation is taken for the synthesis of Elaeocarpus alkaloid which

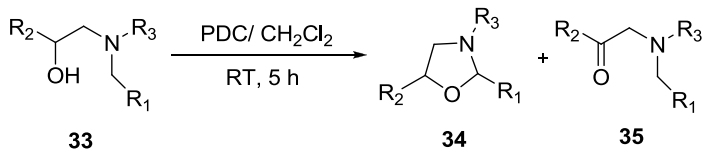
is a large family of indolizidine alkaloids for which iminium ion **30** is used as the common precursor. Reactions of ClO_2 with tertiary amine **28** in presence of excess of aqueous sodium cyanide affording acetal **29**, represents a synthetic equivalent of **30**. By adding a solution of **29**, tryptamine (**31**) and TsOH in EtOH-H_2O to a solution of AgOTs in refluxing EtOH-H_2O, alkaloid (±)-elaeocarpidine (**32**) was generated in moderate yield[74] (Scheme **1.5**).



Scheme 1.5

Oxidation of primary alcohols to aldehydes and secondary alcohols to ketones using pyridinium dichromate (PDC) is a well-established procedure in synthetic organic chemistry. A new reaction was observed by the oxidation of *N*-aryl-*N*-methyl-substituted α-aminoalcohols **33** using PDC to give moderate to

excellent yields of oxazolidines **34** in addition to small amount of ketone **35**[75] (Scheme **1.6**).

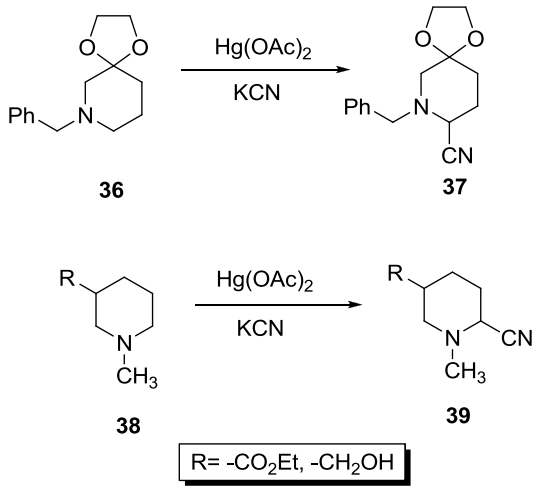


When R_1= H, R_2= 4-$MeOC_6H_4CH_2$, R_3=Ph
34 = 93% and 35 = 4%

When R_1= H, R_2= $PhCH_2$, R_3=Ph
34 = 68% and 35 = 17%

Scheme 1.6

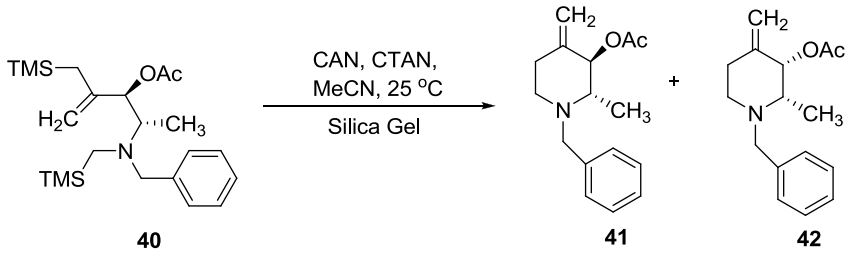
Oxidation of cyclic amines by mercuric acetate to enamines is believed to occur through a two electron reduction of metallic mercury which is subsequently oxidised to mercuric ion by mercurous ions.[76,77] 1-Benzyl-3,3-(ethylenedioxy)piperidine (**36**) and 3- substituted piperidines **38** were regioselectively oxidized by mercuric acetate at the α-position and trapping of the resulting 6-iminium ions with cyanide yielded the corresponding 5-substituted 2-piperidinecarbonitriles **37** and **39**[78] (Scheme **1.7**).



Scheme 1.7

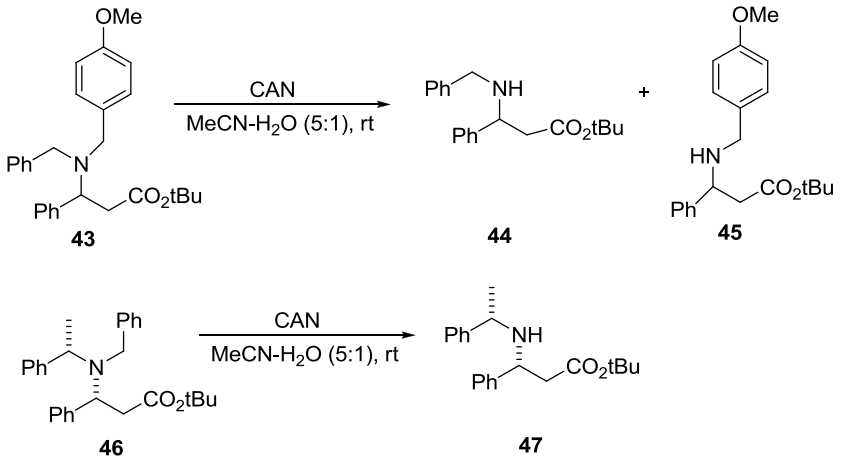
Formation of 3,4'-anhydrovinblastine by ferric ion-induced coupling of catharanthine and vindoline in aqueous acidic media has been proposed *via* the formation of a cation radical of the tertiary amine of catharanthine.[79]

Mannich cyclisation of iminium cations is a convenient method for the synthesis of *N*-heterocyclic compounds.[80] Oxidative Mannich cyclisation of α-silylamines **40** using ceric tetrabutylammonium nitrate (CTAN)[47-49,81] and ceric ammonium nitrate (CAN) has been utilized for the synthesis of hydropyridines **41** and **42** (Scheme **1.8**). α-Silylamides also yielded hydropyridines under the above condition.



Scheme 1.8

When *N*-benzyl tertiary amines are treated with aqueous ceric ammonium nitrate, *N*-debenzylation to yield the corresponding secondary amine is observed.[82] Due to the inherent stability and ease of introduction, the benzyl moiety was commonly used as the protecting group for hetero atom functionality in organic synthesis (Scheme **1.9**) and CAN is effective for the deprotection step.

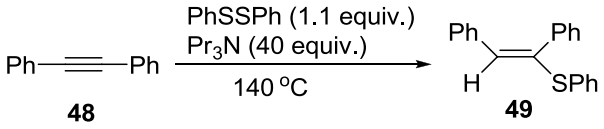


Scheme 1.9

Amine radical cations are major intermediates for one electron transfer reactions. Mixing micromolar solutions of amines with micromolar amounts of $Cu(ClO_4)$ in acetonitrile solution leads to the formation of amine radical cation in good yield.[83] The radical cations thus generated were characterised using absorption and electron spin resonance spectra. Here the radical cations are formed through the donation of an electron from the amines to Cu^{2+}.

Anilines and benzylamines have been utilised to synthesise azobenzenes and *N*-benzylidenebenzylamines in the presence of metal oxide catalysts.[72,84,85]

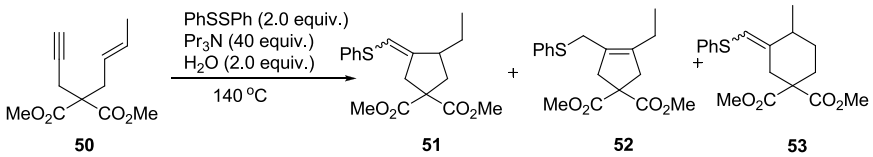
Diphenyldisulphide and tripropylamine react with alkynes to form corresponding hydrothiolated product **49**[86] (Scheme **1.10**).



48 **49**

Scheme 1.10

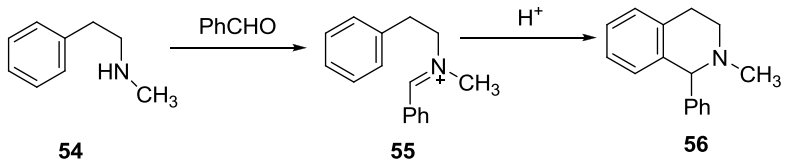
When eneyne compounds **50** react with diphenyldisulphide and tripropylamine, various cyclic products are formed by the amine mediated radical cyclisation[86] (Scheme **1.11**).



50 **51** **52** **53**

Scheme 1.11

One of the most useful methods for the synthesis of *D*-Aryl-fused piperidine ring systems[87] is the Pictet-Spengler reaction. This reaction is an acid catalysed condensation of an arylethylamine **54** with an aldehyde. Intramolecular capture of the intermediate iminium cation **55** by aryl ring leads to the generation of the piperidine ring system **56**[88] (Scheme **1.12**).



54 **55** **56**

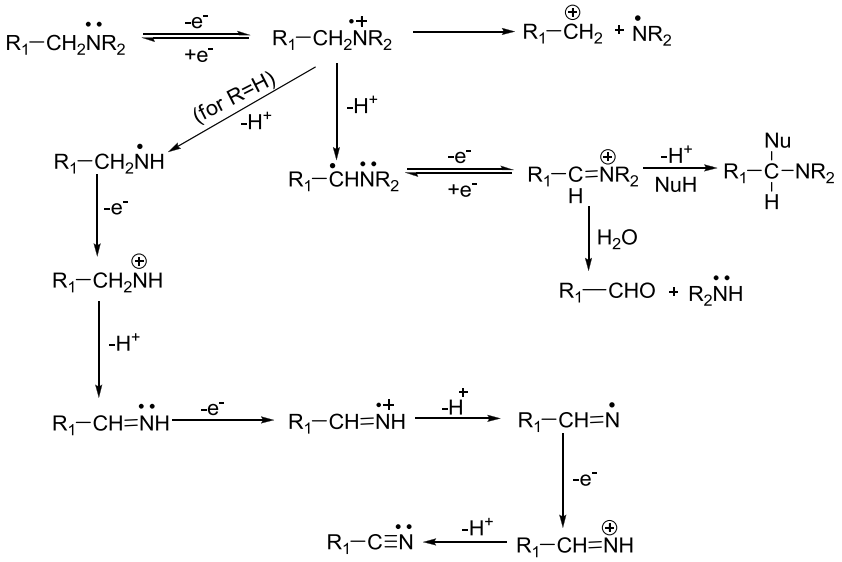
Scheme 1.12

1.3.2. Elelctrochemical Oxidation of Amines and its Synthetic Uses

Elelctrochemical techniques are used for studying one electron transfer reactions of amines.[11] Reaction pattern of anodic oxidation of amines depends on the nature of the electrode and the nucleophilicity of the solvent.[12-14] Major drawbacks of electrode oxidations are unwanted secondary electron transfer reactions that can occur at the electrode surface and the effective volume of the electrochemical reaction limited at the electrode surface, thereby creating a high local concentration of reactive intermediates which can lead to dimerization and disproportionation reactions.

Electrolytic oxidation of aliphatic amines[12-14,89,90] leading to the formation of amine radical cations and various steps involved in

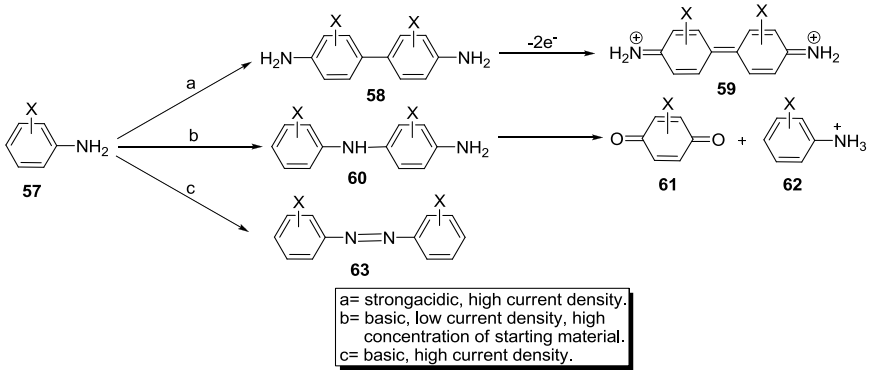
electrolytic oxidations are shown in the Scheme **1.13**.



Scheme 1.13

Anodic oxidation of aromatic amines[12-14,91] is more complex and seriously affected by the reaction condition. Aniline and its derivatives **57** undergo anodic oxidation to give different products and it depends upon the reaction medium.[92] Dimerization followed by deprotonation yielded benzidines **58** and this was favoured under strongly acidic conditions and high current densities. As benzidine is more easily oxidizable than the parent amine, it is converted to the diimine species **59**. 4-Aminodiarylamine **60** was formed in basic solutions at low current densities and high concentration of starting materials. Under this condition deprotonation of **57** was favoured, yielding a resonance stabilized radical followed by C-N coupling with **57** leading to the

formation of **60** and it underwent further oxidation to form *p*-benzoquinone **61** and corresponding anilinium ion **62**. Azo compounds **63** are formed in basic solution by the head-to-head coupling of deprotonated radical (Scheme **1.14**).

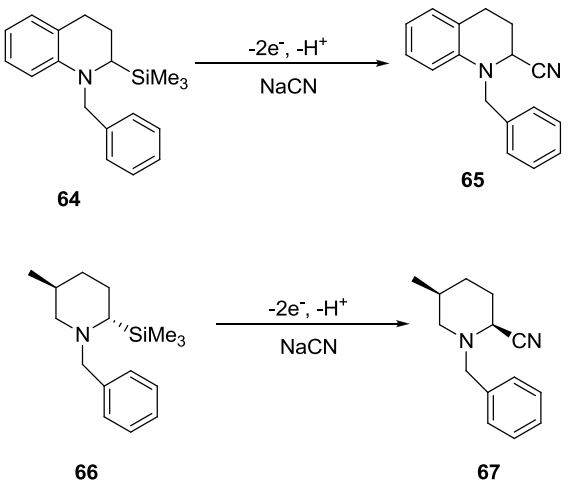


Scheme 1.14

Electrochemical oxidations of amines have many synthetic applications. Nitriles are formed in good yield by the electrochemical oxidation of primary amines using nickel hydroxide electrode by dehydrogenation.[12-14]

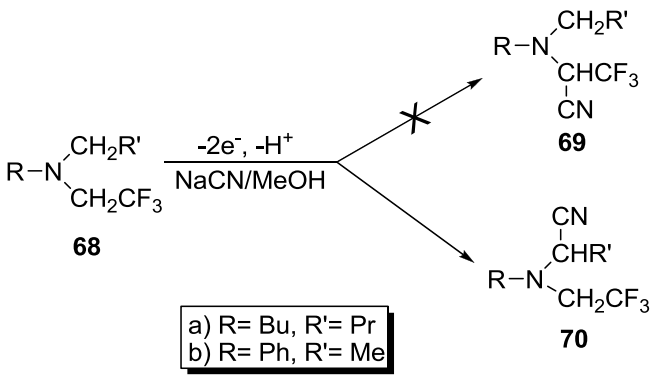
α-Cyanoamines **65** and **67** are formed by the electrochemical cyanation of six membered α-silylamines **64** and **66** respectively. To study the stereoselectivity and regioselectivity of the cyanide addition in silylamines, 3-methylpiperidine (**66**) was taken as the model compound. Only one *cis* diastereoisomer was formed by the addition of cyanide anion onto the iminium species under stereoelectronic control[93] (Scheme **1.15**). Here the cyano group prefers axial position. Hussan and co-workers compared this

preffered orientation to the well-known anomeric effect or Edward-Lemieux effect.[94]



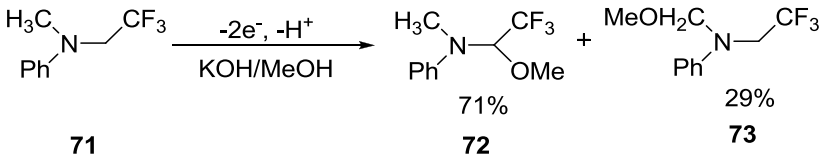
Scheme 1.15

α-Cyanation was also achieved by the electrochemical cyanation of aliphatic tertiary amines and heterocyclic amines in sodium cyanide-methanol solution using platinum electrode. In diphenylamine, cyanation takes place at the para position of one of the phenyl rings. In *N*-methylaniline, the methyl group was cyanated by the electrochemical reaction.[95,96] But in the case of fluorinated amines **68** the cyano group was not introduced at the α-positon of the fluoromethylated carbon atom **69**. Here the cyanation took place at the other α-carbon atom to the nitrogen atom to yeiled **70**[97,98] (Scheme **1.16**). In the case of unsymmetrical amines, generally α-cyanation occurred at the less substituted carbon atom.



Scheme 1.16

In contrast to the cyanation, regioselectivity is completely changed during methoxylation of fluorinated amines. In the anodic methoxylation of fluorinated amines **71**, major product is formed by the introduction of methoxy group at the α-position of the fluoromethylated carbon atom **72**[99] (Scheme **1.17**).

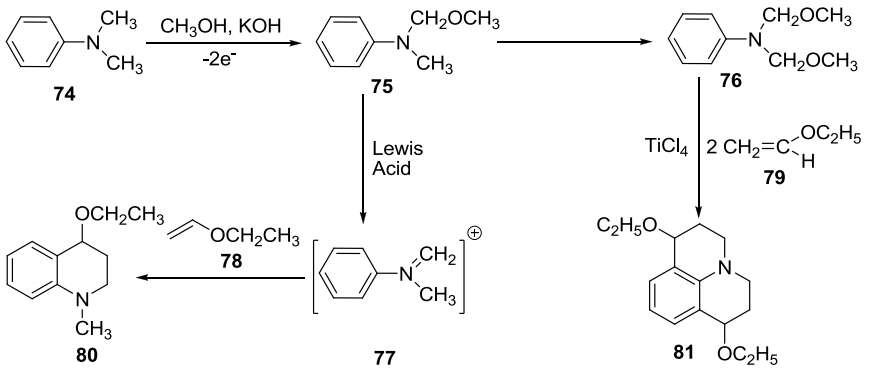


71 **72** **73**

Scheme 1.17

Anodic methoxylation of *N*,*N*-dimethylaniline (**74**) and *N*-methy-*N*-alkylamine **75** in basic methanol gives the methoxylated amine at the less substituted α-carbon atom. Here α-methoxylated *N*,*N*-dimethylaniline **75** and **76** are converted to iminium cation[98] by Lewis acid, which can be trapped in situ by electron rich olefins **78** and **79** and is used for the synthesis of tetrahydroisoquinoline **80**

and julolidine **81** derivatives[100] (Scheme.**1.18**).



Scheme 1.18

1.3.3. Radiation Induced Chemical Studies of Amines

Radiation chemical methods are also used to study the reaction mechanism of amine oxidation.[101-104] Reactive intermediates are derived from solvents by the interaction of ionizing radiation with solvent molecules in dilute solutions. Solvated electrons, hydroxyl radicals, and hydrogen atoms are formed by the radiolysis of dilute solutions. Hydrogen atom formation is negligible in neutral and alkaline solutions.[105]

Pulse radiolysis in combination with optical,[101-104] conductivity[106] and ESR[107,108] detection techniques is used to study the formation and subsequent reaction of amine radical cations formed by radiolysis. In the pulse radiolysis experiment, the transient signals from amine radicals are not complicated by the presence of radical anions. Radical anions are formed along with

the generation of amine radical cations in photoinduced electron transfer processes.[109] Due to the liability of the hydrogen atom attached to the α-carbon atom of the amines, apart from the good electron donors, amines are also good hydrogen atom donors. But the reaction of hydroxyl radical with amine mainly occurs via electron transfer reaction. Pulse radiolysis studies of tertiary amines like trimethylamine and *N*,*N*-dimethylaniline show the formation of addition product with hydroxyl radical and amine. But in the case of aniline, the oxidation by hydroxyl radical forms anilinium radical and after a few seconds it loses a proton to form the neutral radical.[110,111] External base was used for the deprotonation of the anilinium radical because the pK_a value of radical cation is higher than its parent amine.

Unstable radical cations[107,108,112,113] were generated by UV photolysis or γ-radiolysis in strongly acidic solution. These radical cations were examined by ESR spectral studies.[107,108] Radical cations of bulky amines such as triisopropylamine and 9-*tert*-butylazabicyclo[3.3.1]nonane are more stable and are prepared by oxidation in dichloromethane using SbF_5.[114,115]

1.3.4. Photochemical Reactions of Amines and its Synthetic Applications

Nowadays photoinduced electron transfer reactions[15,17-20] are used for many synthetic organic transformations. Amines and its derivatives undergo photoelectron transfer reaction to form

amine radical cations followed by secondary reactions to yield α-aminoalkyl radical, which provides a useful pathway for the synthesis of carbon-carbon bond and many alkaloid derivatives. Redox properties of the electron donor or electron acceptor change during photoexcitation. Upon irradiation, sensitizer molecule gets excited and an electron is transferred from highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The electron from the LUMO can be transferred to the vacuum continuum with less energy than an electron in the HOMO. Therefore the sensitizer molecule behaves as a good electron donor and the vacancy in the ground state of HOMO makes higher electron affinity in the excited state. So the excited state has higher electron donor as well as electron acceptor character relative to its ground state.[116]

Marcus[117,118] correlated the rates of electron transfer reaction with a thermodynamic function ΔG^0. Photoinduced reaction can be endergonic ($\Delta G > 0$) or exergonic ($\Delta G < 0$). According to Marcus, the rate of electron transfer increases as ΔG^0 becomes more exergonic until it reaches a maximum and then begins to decrease with further increase in the driving force.

The overall mechanism involving the electron transfer processes in a fluid medium is the formation of an encounter complex between the excited state and ground state molecule.[119-121] Encounter complex can be described as an intermolecular ensemble of excited and ground state molecule separated by a small distance (~7 Å) and surrounded by solvent molecules. During the lifetime of

the encounter complex, the reactants undergo mutual collisions inside the solvent cage to form collision complex. In the collision complex the reactants are in contact with each other. The collision complex can rapidly be changed to exciplex, if the interaction between the reactant molecules is strong enough. It has partial charge transfer character and large dipole moment. Electron transfer from the collision complex or from the exciplex leads to charge transfer species called contact ion pair (CIP). Solvent separated ion pair (SSIP) can be generated by slight separation of the contact ion pair in the solvent cage. Alternatively, electron transfer from the encounter complex can directly lead to the SSIP. Solvent separated ion pair diffuse out of the solvent cage and get separated to form the free solvated radical ions (FRI), which are analogous to free radicals and can undergo reactions to yield products [116](Figure **1.3**).

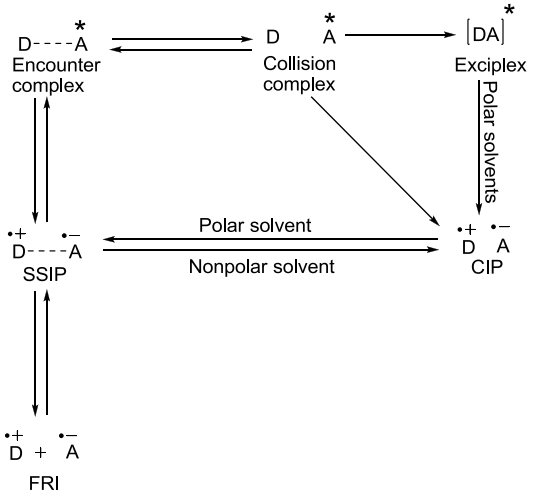


Figure 1.3

In the above process, formation of encounter complex, collision complex, solvent separated ion pairs and free radical ion pairs are reversible. Here we can see the competition between the generation of free radical, which is the forward reaction and the energy wasting back electron transfer. There are many methods used to increase the forward reaction like use of polar solvents, use of triplet sensitizers, use of sacrificial electron donors and mediators, use of ionic species, formation of reactive intermediates and electron transfer at interfaces.[116]

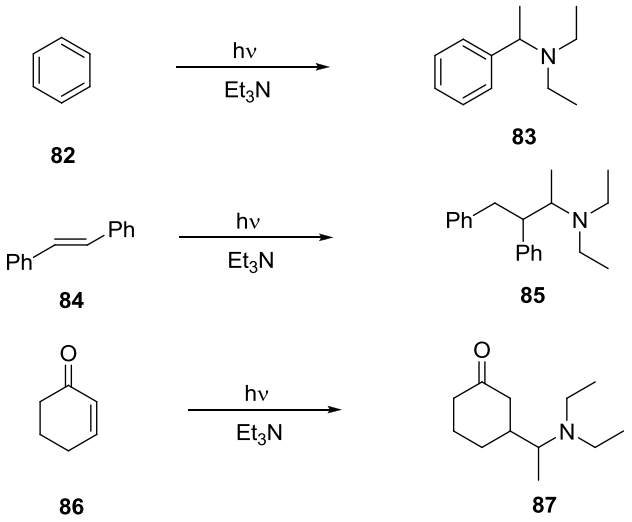
Amines are easily oxidizable due to their low oxidation potential.[122,123] Amine radical cation is formed by one electron oxidation reaction. These are highly reactive and undergo reactions in different modes, namely 1) deprotonation at nitrogen, 2) deprotonation at α-carbon, 3) intra or intermolecular hydrogen abstraction, 4) coupling reaction. Deprotonation at nitrogen occurs by the addition of external base especially in polar aprotic solvent like acetonitrile. Hydrogen atom abstraction and coupling reaction of amine radical cations are less important. The best example for intramolecular hydrogen abstraction is Hoffman-Loffler-Freytag reaction. Intermolecular hydrogen abstraction reaction of amine radical cation occurs at the carbon atom α to the hetero atom. Formation of α-aminoalkyl radical by the deprotonation at the α-carbon is the most common reaction of amine radical cation. For this deprotonation there must be an overlap between the half vacant nitrogen *p* orbital and the σ-CH orbital of the α-carbon. The α-aminoalkyl radical thus formed undergoes different types of

reactions like disproportionation,[124] dimerization,[124,125] oxidation,[122] hydrogen abstraction[123] and carbon-carbon bond formation with olefinic substrates.

Nanosecond and picosecond laser flash photolysis techniques[126] are used to study the mechanism of photoinduced electron transfer process. Using these techniques, formation of collision complex, contact ion pair, free radical ions and free radicals can be monitored.[21]

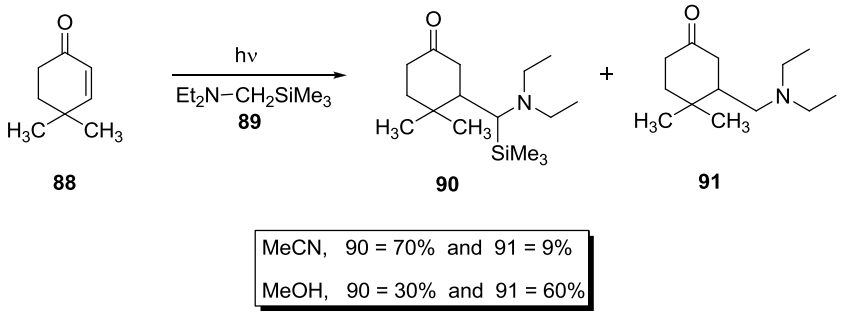
The singly occupied orbital (SOMO) of radicals interacts with the LUMO and/or HOMO of the C=C. Radicals with high SOMO interact preferentially with the LUMO of the alkene. According to frontier molecular theory α-aminoalkyl radicals are nucleophilic in nature and can react very fast with electron withdrawing groups attached to olefinic substrates.[29,127] Electron withdrawing substituents at the olefin lower the LUMO energy and increase the addition rate by reducing the SOMO-LUMO difference.

There has been a wide range of application in synthetic use of the addition of alkene to amines *via* the single electron transfer deprotonation route. Direct excitation of arenes **82**, alkenes **84**, and α,β-unsaturated ketones **86** in the presence of triethylamine leads to the corresponding α-aminoalkyl derived products **83**, **85** and **87**[128-131] (Scheme **1.19**).



Scheme 1.19

Photoreactions of silylated tertiary amines, such as **89** with the cyclohexanone derivative **88** gave trimethylsilyl (TMS) containing adduct **90** and non-TMS adduct **91**[132,133] (Scheme **1.20**).

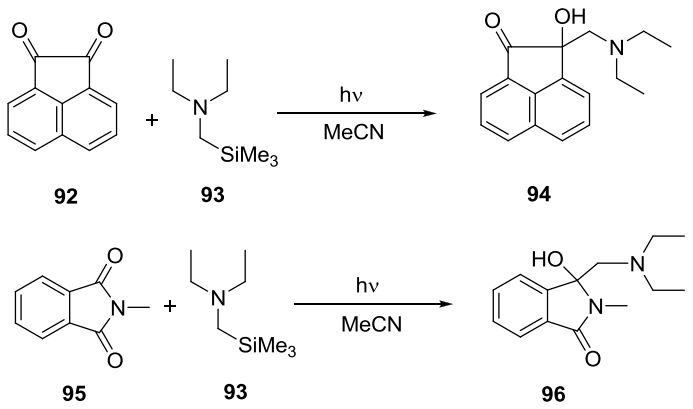


Scheme 1.20

Formation of products **90** and **91** depends on the solvents used in the reaction.[133] If a polar aprotic solvent like acetonitrile

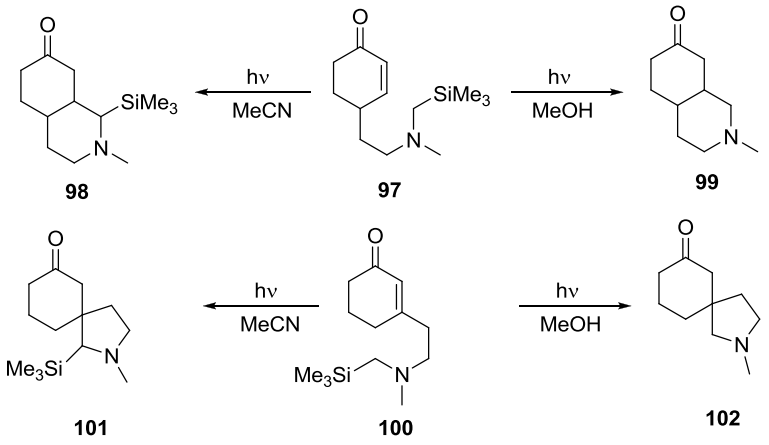
was used, TMS adduct **90** predominates and when polar protic solvent methanol was used, non-TMS adduct **91** predominates. Here the relative rates of amine radical cation deprotonation and desilylation are controlled by the enone radical anion.

However, products formed exclusively by photoreactions of acenaphthenequinone (**92**) and *N*-methylphthalimide (**95**) with silylamine **93** are the non-TMS adducts **94** and **96**. This is due to the fact that radical anions of α-diketones and phthalimides are more acidic than cyclohexanone derivatives[17] (Scheme **1.21**).



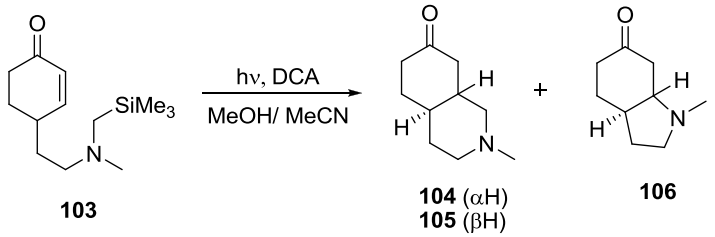
Scheme 1.21

Higher chemoselectivity was observed in the silylamine-enone photocyclization reactions. The cyclized products formed are dependent on the solvent used in the reaction[134,135] (Scheme **1.22**).



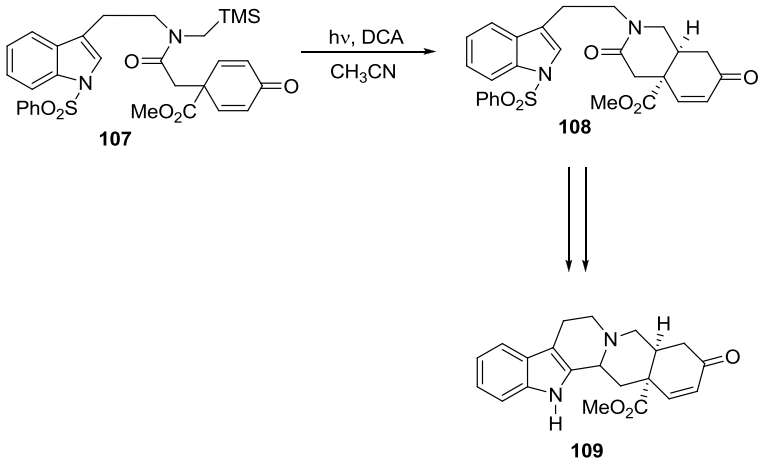
Scheme 1.22

Single electron transfer (SET) sensitized silylamine-enone photocyclization leading to diastereomeric mixtures of products **104** and **105** occurred in the irradiation of dicyanoanthracene (DCA) with **103** in acetonitrile-methanol solution[17] (Scheme **1.23**).



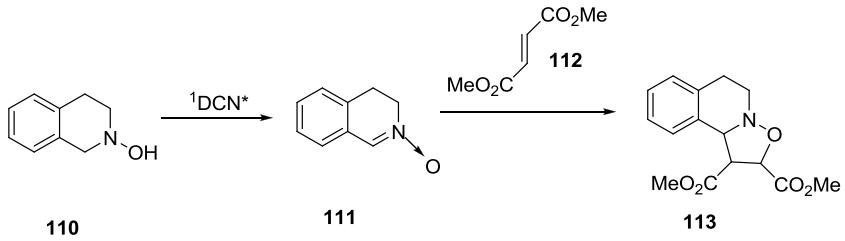
Scheme 1.23

Another synthetic application is the photoinduced radical cyclization of silylamido-cyclohexadienone **107** which is the key step for the synthesis of *E*-ring functionalized alkaloid yohimbane (**109**)[136] (Scheme **1.24**).



Scheme 1.24

Dicyanonaphthalene (DCN) sensitized *N*-hydroxyamines **110** to yield nitrone intermediates **111** and trapping the intermediate by using dimethyl fumarate (**112**) gave corresponding cycloadduct **113** in good yield[137] (Scheme **1.25**).



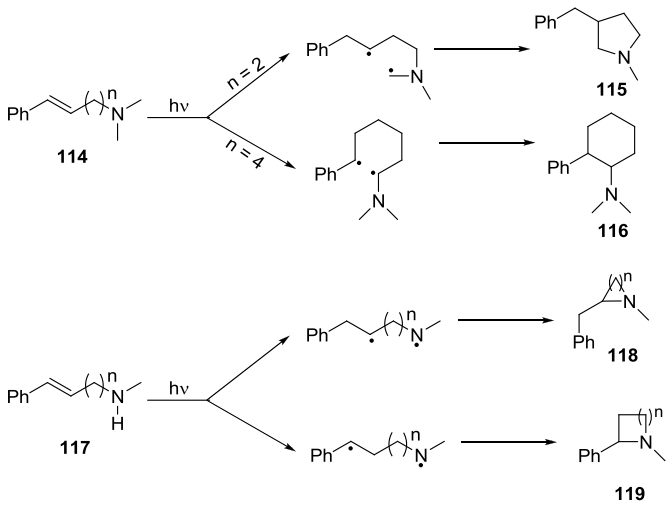
Scheme 1.25

Primary and secondary amines react with α,β-unsaturated esters to form corresponding spirolactams, bicyclolactams and pyrrolidine derivatives by the anthraquinone photosensitized reactions.[138] Michael type adducts are formed by the anthraquinone

photosensitized reactions of secondary amines like pyrrolidine, piperidine and morpholine with α,β-unsaturated esters.[139]

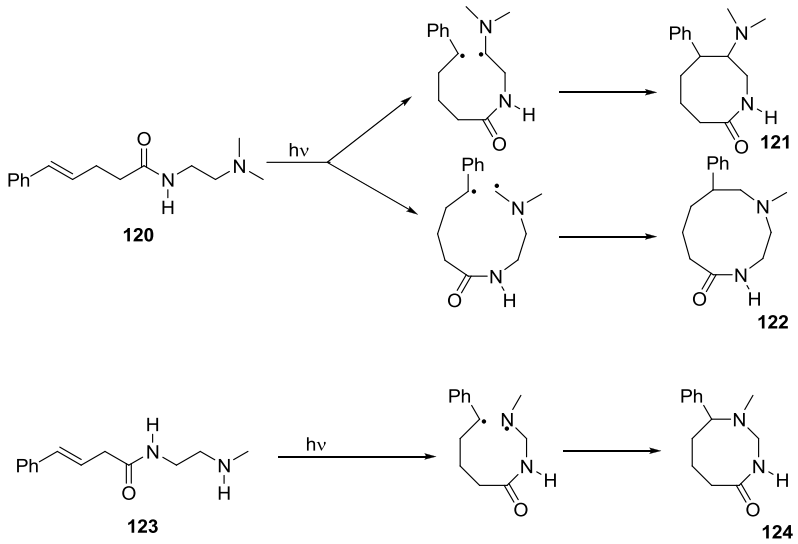
Phenylalkylamines undergo intramolecular photocycliztion to give the *meta*-cyclized product. This is formed through the intramolecular charge-transfer exciplex.[140] But phenanthrene appended anilinoalkylamines undergoe intramolecular photoinduced cyclization in a different manner. Cyclization of the anilino group to the 6,8-, 1,3- and 9- positions of the phenanthrene ring depends on the spacer between the phenanthrene and aniline group.[141]

Tertiary (aminoalkyl)styrenes **114** undergo intramolecular cyclization by α-C-H addition to give either nitrogen heterocycles **115** or aminocycloalkanes **116**, depending on the origin of the α-C-H, whereas secondary (aminoalkyl)styrenes **117** under N-H addition yield nitrogen heterocycles **118** and **119**[142,143] (Scheme **1.26**).



Scheme 1.26

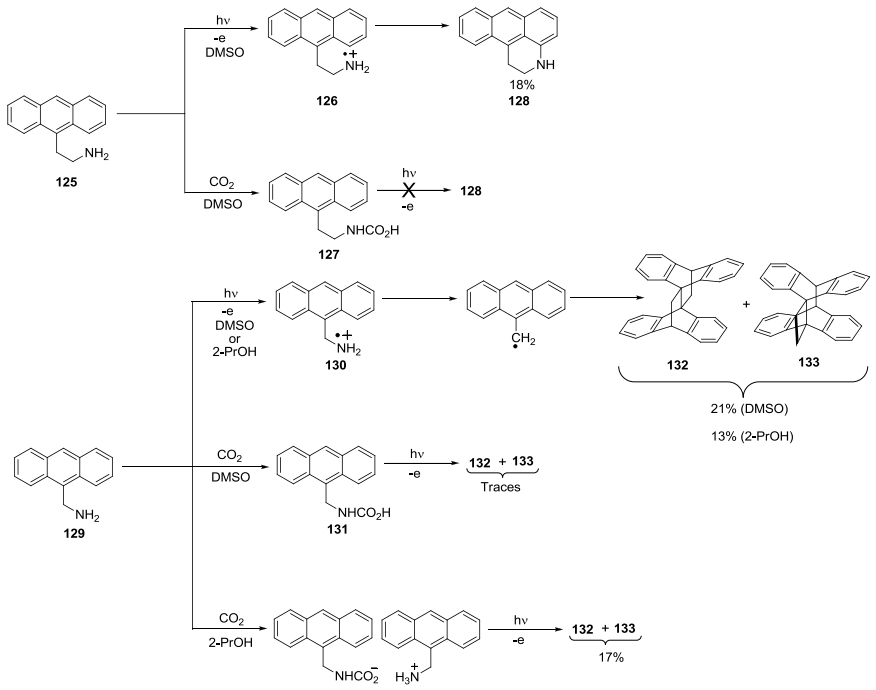
Similarly in the styrene-spacer-amine family the spacer having rigid amide group in the middle of the flexible alkyl chain also shows the intramolecular photoaddition reaction. Here the tertiary amines **120** gave medium ring lactams **121** and **122** and secondary amines **123** yielded azalactam **124**[142-147] (Scheme **1.27**).



Scheme 1.27

Effect of CO_2 and solvent in the photoreaction can be studied by comparing the results obtained by the photoreaction of (9-anthryl)alkylamines **125** and **129**. Reaction was carried out with and without the presence of CO_2 in DMSO and isopropanol. In the case of **125**, the formation of **128**, **132** and **133** are quenched by CO_2. This is due to the formation of carbamic acid **127** and prevented to undergo electron transfer reactions. Also, the products formed in the above reaction depend on the 'spacer' between the

anthracene and amine moiety. In the case of **129**, electron transfer reactions cannot quench under CO_2 in both DMSO and isopropanol.[148] (Scheme **1.28**).



Scheme 1.28

1.4. Michael Addition Reactions

Arthur Michael discovered Michael addition reaction. Generally Michael addition is the efficient coupling of electron poor olefins with a wide variety of nucleophiles.[149] It is also known as 1,4-conjugate addition. Michael addition reaction occurs rapidly

at low temperatures, offers low cure time and involves less toxic precursors.[150]

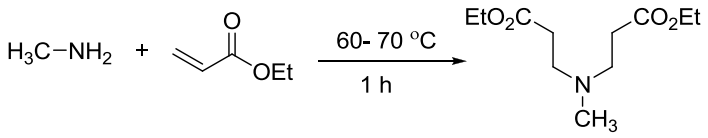
Michael addition reactions usually proceed through the base catalysed addition of a nucleophile such as enolate anion (Michael donor) to an activated α,β-unsaturated carbonyl compound (Michael acceptor). Michael addition carried out in ordinary conditions in the presence of catalysts[151-165]or by refluxing donor and acceptor together is termed classical method of Michael reaction. But reaction carried out under greener conditions[166-168] like microwave irradiation and sonication with or without catalyst is known as non-classical method of Michael reaction. The rate of Michael addition reaction depends on the nature of solvent, substrate and base employed.[169-174]

Depending on the Michael donor, Michael additions are classified into carba-Michael,[175-179] thio-Michael,[180-182] oxa-Michael,[180-182] aza-Michael[151,155-157,159,165-168] and Mukaiyama-Michael reactions.[181,183] In carba-Michael reaction, active methylene group and in thio-Michael reaction, free thiol group in basic media are the Michael donors respectively. In oxa-Michael reaction, free alcohol in basic media and in aza-Michael addition reaction free amine in acidic or basic medium are the Michael donors. In the case of Mukaiyama-Michael reaction silyl enolates are the Michael donors. Commonly used Michael acceptors are α,β-unsaturated ketones, α,β-unsaturated nitriles, α,β-unsaturated nitro compounds and α,β-unsaturated esters.[184,185] In this session only

aza-Michael addition will be discussed since it is more relevant to the research project included in this thesis.

Nitrogen atom is the donor part of the Michael reaction which is termed as aza-Michael reaction. Only a few selected examples are cited here. Additional information is available in several other reviews.[160,180,186,187] Amines can act both as nucleophile and base, therefore no additional base is required in these reactions.[188] Aza-Michael addition follows second order kinetics based on the concentration of the acceptor and amine.

Tertiary amines are formed by the reaction of primary amines with two equivalents of electron acceptors. In some cases the second addition follows the second order kinetics, especially when the concentration of the secondary amine increases. Methylamine (**134**) reacts with two equivalents of ethyl acrylate (**135**) to give corresponding tertiary amine **136**[189] (Scheme **1.29**).

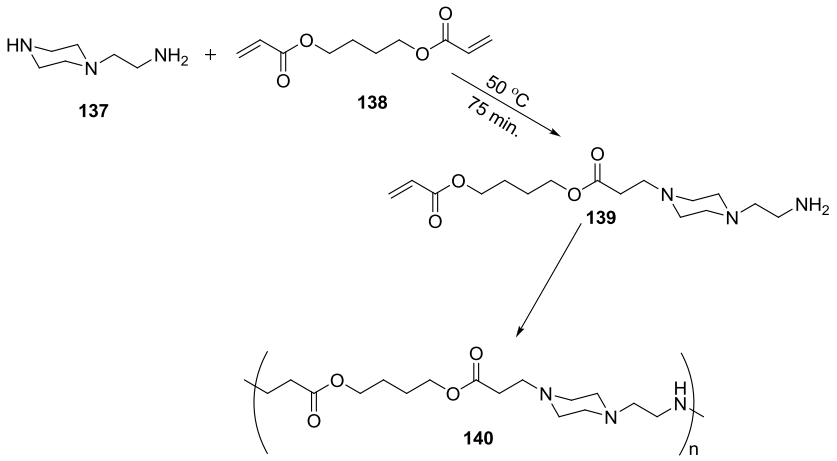


134 **135** **136**

Scheme 1.29

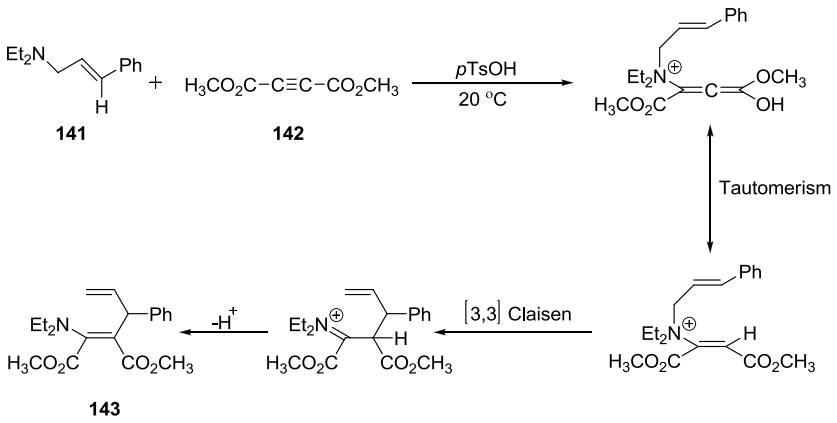
Secondary amines show higher reactivity than primary amines in aza-Michael reaction. This reaction is also dependent on steric and electronic environment of the amine. Reaction of 1-(2-aminoethyl)piperazine (**137**) with 1,4-butanediol diacrylate (**138**) taken in equimolar ratio gives the Michael adduct **139** involving

secondary amine present in the piperazine ring.[190] As the reaction time increases, reaction occurs with primary amine leading to polymer **140** (Scheme **1.30**).



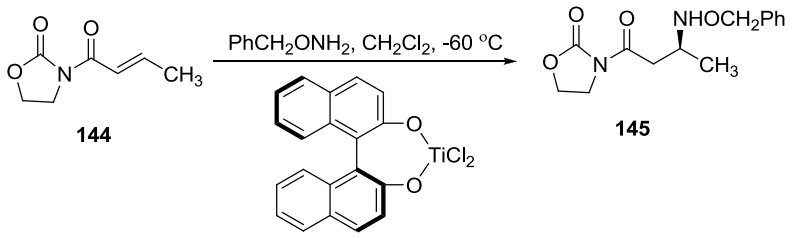
Scheme 1.30

Acid catalysed aza-Michael reactions are studied extensively. When the tertiary amine **141** is added to dimethyl acetylenedicarboxylate (DMAD) (**142**) in the presence of catalytic amount of *p*-toluenesulphonic acid,[191] the resulting intermediate further undergoes Claisen rearrangement to form α,β-unsaturated amine **143** (Scheme **1.31**).



Scheme 1.31

Stereoselective aza-Michael reactions give *β*-aminocarbonyl compounds, which are ubiquitous motifs in natural products and pharmaceutical areas. The $TiCl_2$-BINOL Lewis acid catalyst coordinates with the *N*-acyloxazolidinone (**144**), resulting in the formation of major diastereomer **145** (Scheme **1.32**). The oxazolidinone ring benzyloxy protecting group are then removed to yield the corresponding *β*-amino acid.[192]



Scheme 1.32

Poly substituted chiral 4-aminobenzopyrans bearing three consecutive stereocenters with excellent stereoselectivity can be synthesised by the catalytic asymmetric aza-Michael-Michael

addition of aniline with nitroolefine enolates in the presence of chiral bifunctional thiourea.[151] Many catalysed aza-Michael additions with α,β-unsaturated ketones, carboxylic esters, nitriles and chalcones are discussed in many reviews. [151,155-157,159,165-168.]

Solvent has a major role in the formation of *E* and *Z*-isomers of olefin derivatives by aza-Michael addition reaction. Formations of both *E* and *Z*-adducts by aza-Michael reaction have been reported. Thermodynamic control decides the stereochemistry of the aza-Michael additions. *Z*-isomers have less crowding compared to *E*-isomers. Initially formed *E*-isomers readily isomerise to *Z*-isomers. Protic solvents accelerate the isomerization process.[193,194]

1.5. Diels-Alder Reaction

Otto Diels and his student Kurt Alder published a work in 1928 about the additions of electron deficient alkenes and alkynes to electron rich dienes to form cyclohexenes and cyclohexadienes respectively. These [4+2] cycloadditions are known as Diels Alder reactions. Diels and Alder were awarded the Nobel Prize in Chemistry in 1950 for this work.[195-198]

Diels-Alder reaction is one of the most useful reactions for the formation of carbon-carbon bonds in synthetic organic chemistry. This reaction gives facile, stereospecific entry into six membered rings with one or two double bonds formed in a single step process. Here the electron rich 4π-electron species is called

diene and electron deficient 2π-electron component is dienophile. Electron releasing groups attached to the dienes and electron withdrawing groups attached to the dienophiles increase the rate of Diels-Alder reactions. Diels-Alder additions of conjugated enols and enones to olefinic dienophiles are used for the synthesis of 3,4-dihydro-2*H*-pyranes.[199,200] Azadienes and thiodienes are formed by the cycloaddition of olefinic dienophiles with corresponding heterobutadienes.[201]

According to the Woodward-Hoffmann rules, the concerted suprafacial [$\pi 4_s + \pi 2_s$] cycloaddition of a diene and a dienophile is thermally allowed. As per the above theory, the regioselectivity of the cycloadditions is controlled by either the HOMO of the diene or the LUMO of the dienophile in normal Diels-Alder and by the HOMO of the dienophile or the LUMO of the diene in inverse electron demand Diels-Alder reactions.[202] Woodward-Hoffmann rules give an idea about the transition states of Diels-Alder addition and it can have diradicaloid as well as zwitterionic transition states.[203]

The stereoselectivity of Diels-Alder reaction is high because it requires a cisoid conformation for the diene and suprafacial-suprafacial mode of reaction, which means both ends of the diene attack from the same face of the dienophiles in a *syn* fashion. This principle is known as *cis* principle. Diels-Alder reaction between a dienophile and and a diene commonly give *endo* products.[204,205] The polarizability of the diene and dienophile creates dispersive forces making the *endo* transition state more

stable than the *exo* transition state. Secondary orbital overlap is also possible in this transition state which gives secondary binding forces and it stabilizes the *endo* transition state.[206-210] This *endo* rule was proposed by Alder and Stein.

Diels-Alder reaction was catalysed by adding Brönsted and Lewis acids.[211] Like acids, copper salts[201] and enzymes[212] are also used to catalyse the Diels-Alder reaction. Diels-Alder reactions are classified as homo and hetero Diels-Alder reactions.[213] In homo Diels-Alder additions, carbon-carbon bond formation takes place and in hetero Diels-Alder cyclization bond is formed between carbon and hetero atoms like oxygen, nitrogen, phosphorous or sulphur forming corresponding heterocycles.

Hetero Diels-Alder reactions are mainly used for the synthesis of heterocycles and natural products.[214-216] In these reactions, the imino Diels-Alder reactions gave the functionalized rings with control of regio-, diastereo- and enantio-selectivity.[217-221] Many studies reveal that the rate of Diels-Alder reaction depends on the solvent polarity, concentration and pressure of the reaction medium.[222-226]

Diels-Alder reaction can be conducted in the intramolecular mode. Intramolecular Diels-Alder (IMDA) reaction is subdivided in to two Type I and Type II. Type I means the tether attached to the diene moiety in the first position and type II refers the tether is attached to the second position (Figure **1.4**). The IMDA reactions are gainfully employed for the total synthesis of many natural products.[216]

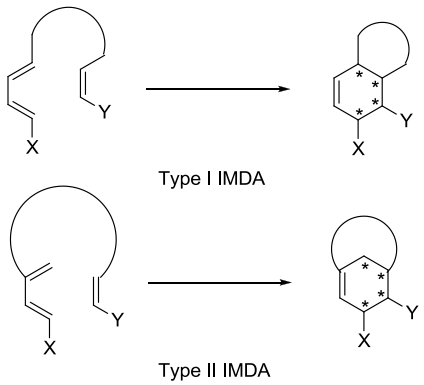
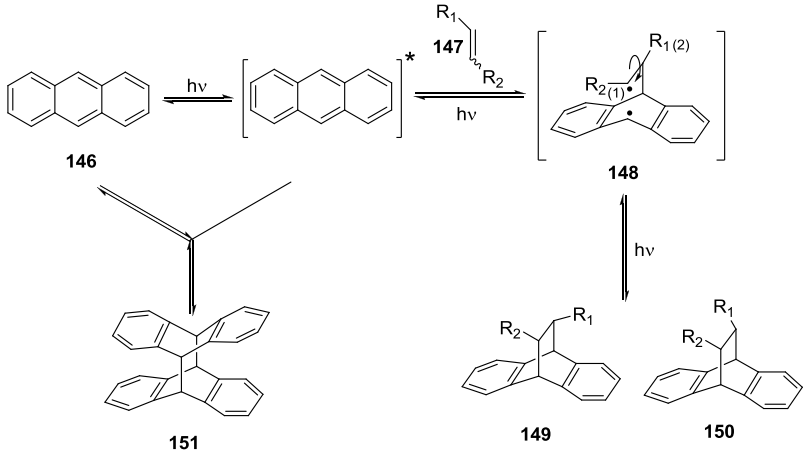


Figure 1.4

Anthracene and its derivatives very easily undergo both thermal and photochemical Diels-Alder addition with a variety of dienophiles across 9 and 10 positions.[227,228] Stereochemistry of the reaction involves the *cis* addition of dienophile to the anthracene ring and *cis* or *trans* stereochemistry of the dienophile is retained in the product.[229] Many groups have studied the solvent dependency of the Diels-Alder reactions involving anthracenes.[227-232] Electron donating ability of the solvent decreases the rate of the reaction by increasing the dissolution of the dienophile.[233] Electron withdrawing solvents stabilize the transition state, which is electron rich in nature.[231,233] Temperature and substituents also affect the rate of the Diels-Alder reaction. Electron releasing groups attached to the 9 and 10 positions of anthracene accelerate and bulky groups attached to the ring decelerate the Diels-Alder reaction.[227,234,235] Here the dienophile has Lewis acid character and substituent effectswere examined by changing their π acceptor character.[236,237]

Photochemical transformations anthracene and 9-substituted anthracenes have been extensively reviewed.[238-240] According to

Woodward-Hoffmann rules, under photochemical conditions, [4+4] concerted cycloadditions are allowed and [4+2] concerted cycloadditions are symmetry forbidden.[241-242] Photocycloaddition of anthracene (**146**) to dienophile **148** is stepwise process.[243] A detailed study of the above reaction reveals that use of high energy UV irradiation results in photoinduced electron transfer in anthracene (**146**) via singlet state **146*** that readily reacts via biradical mechanism with dienophile **147** to form corresponding cycloadducts **149** and **150**. Intermediate **148** undergoes free C-C rotation to form exclusively more stable *trans* adduct **149** indicating non-concerted nature of the observed "cycloaddition" reaction (Scheme **1.33**).



Scheme 1.33

1.6. Boundary delineation of the research problem

It is obvious from the literature survey that amines show electron transfer processes involving one electron, two electrons and Diels-Alder reactions depending on substrate structure and nature of solvents, concentration and temperature. Our interest was to study the solvent dependency, effects of concentration and temperature on one electron transfer, two electrons transfer, Hofmann-Loffler-Freytag type and Diels-Alder reaction in a unique class of tertiary amines. The study is more effective only if the series of reactions was done in a single system.

Not all amines show these three types of electron transfer reactions in a single molecule. For this study we have selected (anthracen-9-yl)methylamines and (bisanthracen-9-yl)methylamines. These tertiary amines can potentially undergo intermolecular electron transfer reactions like one electron transfer, two electrons transfer and Diels-Alder reaction with suitable electron acceptors. To study the effect of electron acceptors in the above reactions, we have selected three types of dienophiles having different electron withdrawing character *viz* dimethyl acetylenedicarboxylate (DMAD), dibenzoylacetylene (DBA) and dibenzoylethylene (DBE). By synthesizing different types of (anthracen-9-yl)methanamines we can easily study the effect of electronic and steric environment around the nitrogen atom in the thermal reactions. Solvent, concentration and temperature dependency in the reactions of amines with different dienophiles

can be studied by selecting nonpolar, polar aprotic and polar protic media. We can perceive interesting competitive reactions in these 'donor-acceptor' interactions including both one and two electron transfer reaction and Diels-Alder reactions between tertiary amines and dienophiles. Also we can examine how these competitive reactions depend on substrate structure, concentration and solvent used in the reactions. Steric factors, for instance, can inhibit nucleophilic addition pathway. This assumption is based on the well-known application of non nucelophilic bases such as DIEA and LDA in organic synthesis.

Interesting photoinduced electron transfer reactions can be studied by the 'donor-spacer-acceptor' type (anthracen-9-yl)methanamines and (bisanthracen-9-yl)methanamines. Upon irradiation these amines show quenching of fluorescence by intramolecular electron transfer and this leads to the cleavage of bonds and dimerization. Along with these products one electron transfer products are obtained. Fluorescence quenching was dependent on the electronic and steric environment around the nitrogen atom which in turn reflects on reaction rate.

Diels-Alder adducts formed by the reaction of (anthracen-9-yl)methanamines and (bisanthracen-9-yl)methanamines with suitable electron acceptors may exhibit interesting photochemical transformations. The dibenzobarrelenes and bisdibenzobarrelenes derived by above reactions contain tertiary amines. Generally, tertiary amines are well known singlet quenchers. Intramolecular singlet quenching through electron transfer is a distinct possibility

here. Another possibility is electron transfer mediated retro Diels Alder reaction. We propose to examine the photochemistry of these amine appended dibenzobarrlelenes to reveal the major reaction course followed by these molecules.

1.7. Objectives

1. Synthesis of tertiary amines
   - ♣ Synthesis of (anthracen-9-yl)methanamines
   - ♣ Synthesis of (bisanthracen-9-yl)methanamines
2. Synthesis of dienophiles
   - ♣ Synthesis of dibenzoylacetylene
   - ♣ Synthesis of dibenzoylethylene

3. Study the reactions of (anthracen-9-yl)methanamines and (bisanthracen-9-yl)methanamines with dienophiles in different solvents
   - ♣ Non polar medium – Xylene
   - ♣ Polar aprotic media – Acetonitrile, Dimethylformamide
   - ♣ Polar protic media – a) Acid, Acetic acid
     b) Alcohol, Methanol

4. Explore the photoinduced electron transfer reactions in (anthracen-9-yl)methanamines and (bisanthracen-9-yl)methanamines

5. Examine the photoinduced electron transfer reactions in 9-aminomethylanthracene derived dibenzobarrelenes and bisdibenzobarrelenes

6. Study the mechanism of the above thermal and photochemical reactions

1.8. References

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CHAPTER 2

SYNTHESIS AND CHARACTERISATION OF A FEW (ANTHRACEN-9-YL)METHANAMINES

2.1. Abstract

Our aim is to synthesise a series of suitable substrates capable of undergoing competing one electron transfer, Michael type addition and Diels-Alder reactions with suitable electron acceptors. In this chapter, we describe the synthesis of a few (anthracen-9-yl)methanamines which can potentially undergo competing electron transfer reactions. These molecules also show photoinduced intramolecular electron transfer reactions.

2.2. Introduction

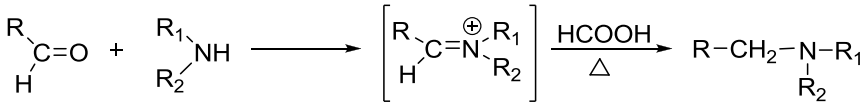
Amines are used in several electrochemical,[1-3] photochemical[4-12] and biochemical redox processes[13-16] because the lone pair of electrons on the nitrogen atom of amines are very easy to oxidise. One electron oxidation of amines leads to the formation of amine radical cations and these cations can be used for the synthesis of several amino acids, alkaloids and nitrogen

containing compounds having pharmaceutical and biological importance.[17-19] Amines also act as a donor for Michael addition reactions with suitable electron acceptors. These reactions are called aza-Michael additions.[20-24] Hence the electron transfer reactions of amines are very important.

Anthracene and its derivatives are well known dienes in Diels-Alder reactions. They readily undergo both thermal and photochemical Diels-Alder addition with a variety of dienophiles across 9 and 10 positions.[25] We selected (anthracen-9-yl)methanamines for studying competitive electron transfer reactions including one electron transfer, Michael addition and Diels-Alder reaction with suitable dienophiles. These amines have anthracene-spacer-amine geometry. Since the methylene spacer effectively shuts the electronic communication between amine and anthracene component in the ground state, amine part of the (anthracen-9-yl)methanamines can easily undergo one electron transfer and Michael addition reactions whereas anthracene part shows Diels-Alder reaction with suitable electron acceptors. Thus, the proposed molecules can react independently as an anthracene or a tertiary amine and exhibit photophysical characteristics analogous to those of 9-alkyl substituted anthracenes.

We have synthesised the (anthracen-9-yl)methanamines by using Leuckart and nucleophilic substitution reactions. Leuckart reaction was first discovered by Rudolf Leuckart in 1885[26]. It is a process for the reductive alkylation of ammonia or primary or secondary amines by certain aldehydes and ketones, in which

formic acid or a derivative of formic acid serves as the reducing agent.[27-30] Several modifications of original Leuckart reaction appear in later literature.[31-34] Amides are also used instead of amines in Leuckart reaction when formic acid is used as the reducing agent.[31] General mechanism[35] for the Leuckart reaction is presented in Scheme **2.1**.



Scheme 2.1

Leuckart reaction has many synthetic applications.[36-39] One of the main applications is the synthesis of amphetamines[40] and methamphetamines,[41] which are stimulant drugs that speed up the body's central nervous system. It is also used in the synthesis of tetrahydro-1,4-benzodiazepin-5-ones,[42] γ-phenylpropylamines,[34] dimethylaminomethyl derivatives of polycyclic aromatic hydrocarbons[43] and 1-methyl or 3-hydroxymethyl-1,3-heterocycles.[44]

Amines can react as nucleophiles with alkyl or aryl halides in substitution reactions. Nucleophilicity of amines is controlled by both the base strength and size of amines used.[45] According to Brady and Cropper,[46] amines with a number of alkyl groups on or near their nitrogen atoms are in general less reactive than amines with less branching near the nucleophilic centre. It appears that steric factors are more important than base strength in controlling

nucleophilicity of amines. Consequently, non-nucleophilic bases such as DBU and DIEA are commonly encountered in organic synthesis. However, relatively unhindered amines act as good nucleophiles in several reactions. Here we have employed nucleophilic substitution reaction of amines for the synthesis of a few (anthracen-9-yl)methanamines.

2.3. Results and Discussion

With an aim to examine chemoselectivity, solvent and concentration dependency of the reaction of tertiary amines with Michael acceptors such as α,β–unsaturated carbonyl compounds, we have synthesised a few (anthracen-9-yl)methanamines **1a-h** employing either Leuckart reaction protocol or nucleophilic substitution on suitable secondary amines (Figure **2.1**).

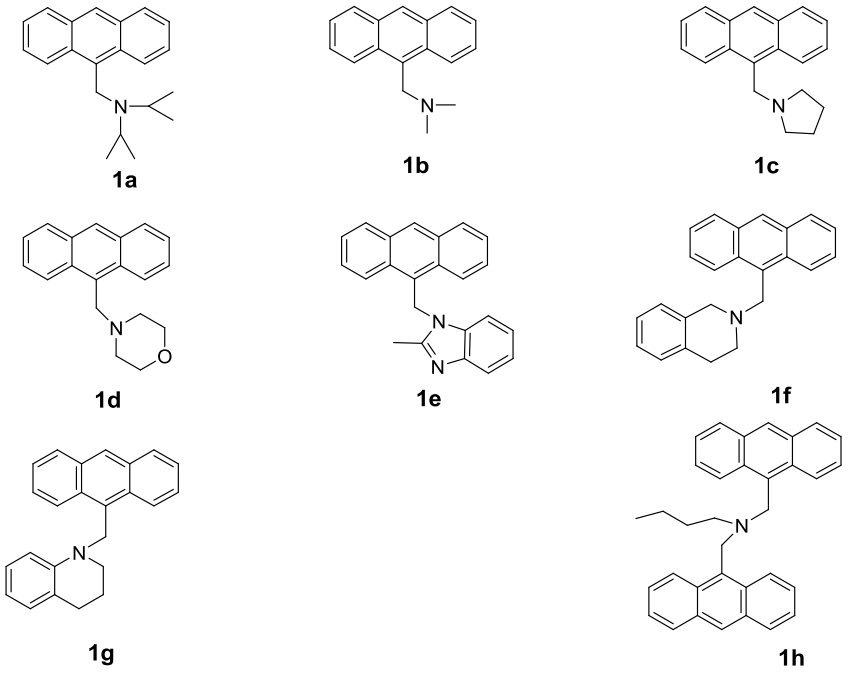
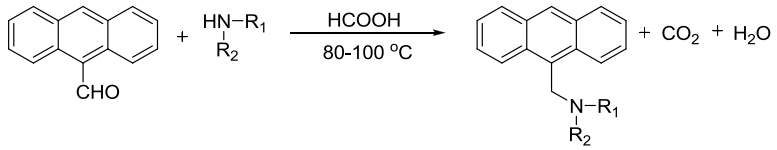


Figure 2.1

Leuckart reaction was used for the synthesis of above (anthracen-9-yl)methanamines except **1e**. Here refluxing 9-anthraldehyde (**2**) with corresponding secondary amines in the presence of formic acid yielded the corresponding (anthracen-9-yl)methanamines in good yield. General method for the above reaction is represented in Scheme **2.2**. Reaction temperature and time were modulated according to the secondary amines used in the reactions.

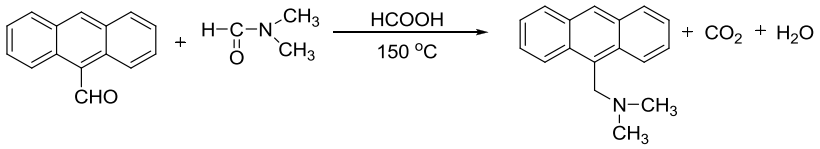


3a, 3c, 3d, 3f, 3g, 3h | **1a, 1c, 1d, 1f, 1g, 1h**

2

Scheme 2.2

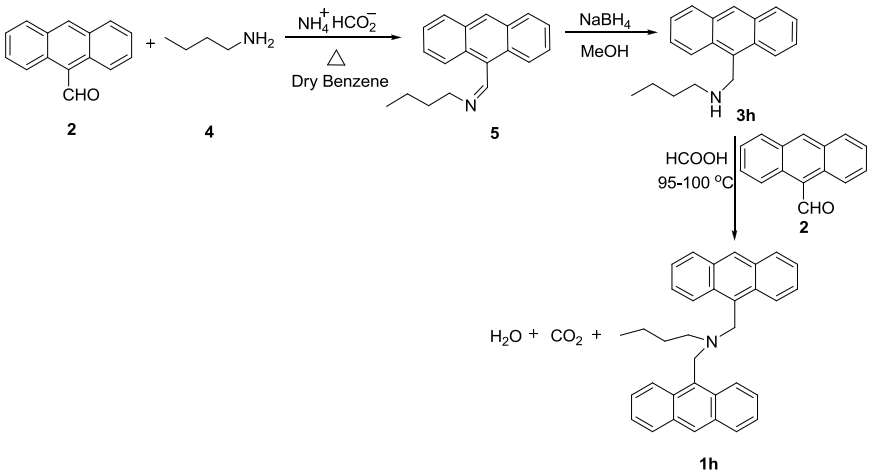
We have used Leuckart-Wallach modification[31] for the synthesis of 9-(*N*,*N*-dimethylaminomethyl)anthracene (**1b**). In this modification *N*,*N*-dimethylformamide (DMF) (**3b**) was used instead of secondary amines (Scheme **2.3**).



2 **3b** **1b**

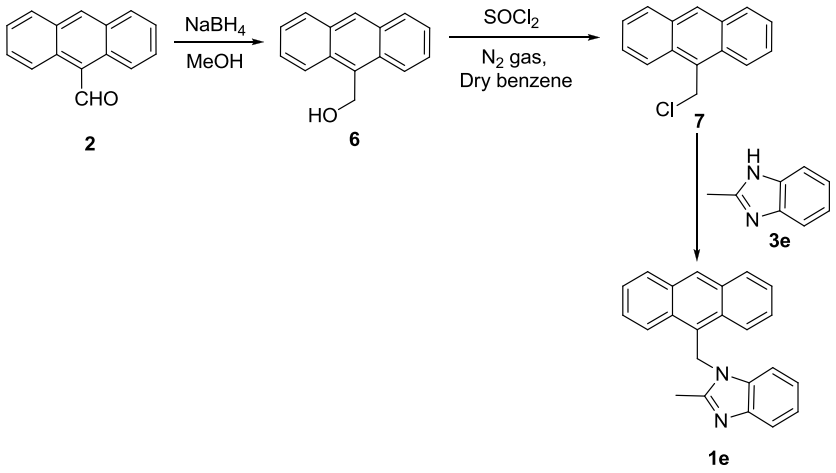
Scheme 2.3

One-pot Leuckart reaction[47] with 9-anthraldehyde (**2**) and *n*-butylamine (**4**) followed by $NaBH_4$ reduction was used for the synthesis of (*N*-butylaminomethyl)anthracene (**3h**). This secondary amine **3h** on refluxing with 9-anthraldehyde (**2**) in the presence of formic acid gave 9-(*N*,*N*-bisanthracenemethyl)butylamine (**1h**) (Scheme **2.4**).



Scheme 2.4

We employed nucleophilic substitution reaction on 9-chloromethylanthracene (**7**) with 2-methylbenzimidazole (**3e**) for the synthesis of *N*-((anthracen-9-yl)methyl)-2-methylbenzimidazole (**1e**). Here, 9-anthracenemethanol (**6**) was treated with thionyl chloride ($SOCl_2$) in dry benzene under inert condition at room temperature (RT) for 1.5h followed by reflux at 80 °C for half an hour yielding 9-chloromethylanthracene (**7**). We synthesised 9-anthracenemethanol (**6**) by the reduction of 9-anthraldehyde (**2**) with $NaBH_4$ in methanol. Since **7** was highly reactive, no attempts were made to purify it. Direct addition of 2-methylbenzimidazole (**3e**) to crude **7** at room temperature gave *N*-((anthracen-9-yl)methyl)-2-methylbenzimidazole (**1e**) (Scheme **2.5**).



2 6 7 3e 1e

Scheme 2.5

Analytically pure samples were obtained by recrystallization from apposite solvent mixtures like hexane-ethyl acetate and DCM-methanol. Based on spectral and analytical data, we confirmed the formation of (anthracen-9-yl)methanamines **1a-h**.

A pertinent question here is: why did we select **1a-h** for our investigation? Close examination of the structural features of **1a-h** reveals the diversity in their structure and reactivity. We summarize our agenda in Table **2.1**.

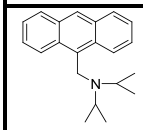
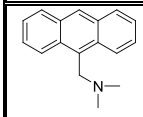
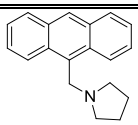
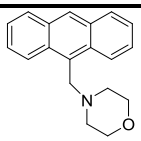
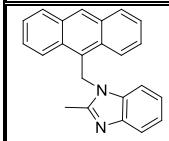
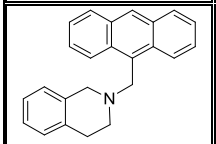
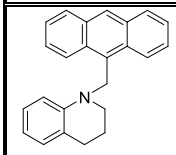
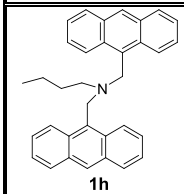
Compound	Significant Feature	Remarks
 1a	Diisopropylamine appended anthracene is like Hunig's base. It may favour radical reactions over nucleophilic addition.	Enhance solubility, Reduce nucleophilicity thereby reduce Michael addition.
 1b	This amine is the lowest member of the family.	To study the nature of steric and electronic effects around the nitrogen atom.
 1c	Here nitrogen atom is a part of a ring.	To study the reaction of anthracenemethanamine having nitrogen atom as part of a ring.
 1d	Nirogen atom is a part of a ring and this ring contains an oxygen atom.	Trans annular interaction is possible between nitrogen and oxygen, this may affect the forward and back electron transfer rates
 1e	Nitrogen atom is a part of an aromatic ring.	Availability of lone pair electrons reduced when nitrogen atom is a part of an aromatic ring. Hence we have to study, how it affect the fluorescence quenching and ET reactions.
 1f	Significant amine component having available lone pair electrons.	In the thermal and photochemical reactions it may be possible to trace out the amine moiety.
 1g	Significant amine component and having less availability of lone pair electrons.	Decreased availability of electrons on the significant amine component may drive the reaction in another direction.
 1h	Significant amine component and suitable for studying Hofmann-Loffler-Freytag reaction.	Butyl group present on nitrogen atom enables Hofmann-Loffler-Freytag reaction

Table 2.1

2.4. Experimental Section

2.4.1. General Techniques

All reactions were carried out using oven dried glasswares. All experiments were done with distilled and dried solvents by using standard protocols. All starting materials were purchased from either *Sigma-Aldrich* or *Spectrochem Chemicals* and were used without further purification. Progress of the reaction and chromatographic separations were monitored by dried and activated silica gel TLC plates (Aluminium sheets coated with silica gel, *E. Merck*). Visualisation of TLC plates was acquired by exposure to iodine vapours or UV lamp. Separation and purification of compounds were done by column chromatography using either silica gel (*Spectrochem Chemicals*, 60-120 mesh) or neutral alumina (*Spectrochem Chemicals)*. The products were further purified by recrystallization from suitable solvent systems. Solvent eluted from the column chromatography was concentrated using *Heidolph* rotary evaporator. Melting points are uncorrected and were determined on a *Neolab* melting point apparatus. Infra-red spectra were recorded using *Jasco 4100* and *ABB Bomem (MB Series)* FT-IR spectrometers. The ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz *Bruker Avance III* FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS. Elemental analysis was performed using *Elementar Systeme (Vario*

EL III). Molecular mass was determined by electron impact (EI) method using GC-MS (*Agilent GC-7890A, Mass-5975C*) and fast atom bombardment (FAB) using *JMS 600 JEOL* mass spectrometer.

2.4.2. 9-Anthracenemethanol:-

9-Anthracenemethanol (**6**) was prepared using a known procedure[48] (60%, mp 158-162 °C).

2.4.3. 9-Chloromethylanthracene:-

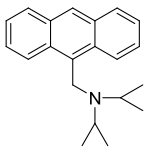
9-Chloromethylanthracene (**7**) was prepared by a known method[48] (84%, mp 136-138 °C) and was used without further purification.

2.4.4. Synthesis of (Anthracen-9-yl)methanamines:-

2.4.4.1. 9-(*N,N*-Diisopropylaminomethyl)anthracene (1a).

Formic acid (1.00 mL, 27 mmol) was mixed with *N,N*-diisopropylamine (**3a**) (6.30 mL, 45 mmol) at room temperature and the mixture was rapidly cooled in an ice bath. 9-Anthraldehyde (**2**) (3.00 g, 15 mmol) was added to the reaction mixture and the flask was heated at 80 °C when rapid evolution of carbon dioxide

was observed. After the evolution stops the solution was refluxed for 10h. The reaction mixture was poured into water and extracted with DCM. 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 passed through a neutral alumina column to remove unreacted **2** (10%) using a mixture of (9:1) hexane and DCM. The yellow solid obtained upon the removal of solvent was recrystallized from a mixture (2:3) of DCM and methanol to separate pure **1a** (79%).



mp:- 129-132 °C.[49]

IR ν_{max} (KBr):- 3051 (=C-H stretch), 2959 (-C-H stretch), 1350-1000 (C-N and C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$):- δ 7.25-8.68 (m, 9H), 4.67 (s, 2H), 2.94-3.03 (m, 2H), 1.14 (d, 12H, *J* = 8.8 Hz).

^{13}C NMR ($CDCl_3$):- δ 131.89, 131.77, 131.55, 128.01, 127.05, 125.41, 125.04, 124.80, 46.71, 41.47, 21.05.

MS:- *m/z* 291 (M^+), 191.

Elemental analysis calculated for

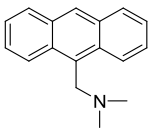
$C_{21}H_{25}N$:- C: 86.55, H: 8.65, N: 4.81.

Found:- C: 86.54, H: 8.66, N: 4.80.

2.4.4.2. 9-(*N,N*-Dimethylaminomethyl)anthracene (1b).

Formic acid (0.80 mL of 90% solution) was added to a sol--ution of 9-anthraldehyde (**2**) (3.00 g, 15 mmol) in 15 mL of dry DMF (**3b**) and stirred under reflux for 12h. After the reaction, the

reaction mixture was poured to water, extracted with DCM and separated. The organic layer was dried over anhydrous Na_2SO_4 and concentrated. The crude residue when passed through a neutral alumina column using a mixture of (9:1) hexane and DCM resulted pure 9-(*N*,*N*-dimethylaminomethyl)anthracene (**1b**) (82%). Since the melting point of **1b** is very low, it exists in liquid form after workup. But we can easily solidify by keeping it in freezer.



mp:- 66-68 °C.

IR ν_{max} (KBr):- 3045 (=C-H stretch), 2928 (-C-H stretch), 1350-1000 (C-N and C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$):- δ 7.49-8.55 (m, 9H), 4.32 (s, 2H), 2.23 (s, 6H).

^{13}C NMR ($CDCl_3$):- δ 130.97, 130.61, 130.44, 128.71, 127.03, 125.60, 125.04, 124.97, 54.31, 45.05.

MS:- *m/z* 235 (M^+), 191.

Elemental analysis calculated for

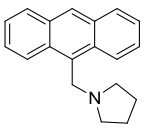
$C_{17}H_{17}N$:- C: 86.77, H: 7.28, N: 5.95.

Found:- C: 86.78, H: 7.27, N: 5.95.

2.4.4.3. *N*-((Anthracen-9-yl)methyl)pyrrolidine (1c).

At RT, formic acid (1.00 mL, 27 mmol) was mixed with pyrrolidine (**3c**) (3.70 mL, 45 mmol) and the mixture rapidly cooled in an ice bath. 9-Anthraldehyde (**2**) (3.00 g, 15 mmol) was added to the reaction mixture and the flask heated at 80 °C. Rapid evolution of carbon dioxide was observed. After the evolution

stopped the solution was refluxed for 8h. The reaction mixture was poured into water and extracted with DCM. The separated organic layer was washed with water and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the solid obtained passed through a neutral alumina column to remove charred materials using a mixture of (9:1) hexane and DCM. The yellow solid obtained upon the removal of solvent and it was recrystallized from a mixture of (2:3) of DCM and methanol to separate pure **1c** (84%).



mp:- 108-110 °C.

IR ν_{max} (KBr):- 3054 (=C-H stretch), 2789 (-C-H stretch), 1350-1000 (C-N and C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$):- δ 7.43-8.53 (m, 9H), 4.58 (s, 2H), 2.64-2.68 (m, 4H), 1.72-1.75 (m, 4H).

^{13}C NMR ($CDCl_3$):- δ 134.11, 131.50, 130.92, 128.95, 127.09, 125.45, 125.05, 124.77, 54.28, 51.38, 23.63.

MS:- *m/z* 261 (M^+), 191.

Elemental analysis calculated for

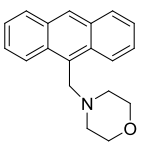
$C_{19}H_{19}N$:- C: 87.31, H: 7.33, N: 5.36.

Found:- C: 87.25, H: 7.38, N: 5.37.

2.4.4.4. *N*-((Anthracen-9-yl)methyl)morpholine (1d).

Formic acid (1.00 mL, 27 mmol) was mixed with morpholine (**3d**) (3.90 mL, 45 mmol) at RT and the mixture was rapidly cooled in an ice bath. To this, 9-anthraldehyde (**2**) (3.00 g,

15 mmol) was added and the flask heated at 80 °C. Rapid evolution of carbon dioxide was observed. After the evolution stopped, the solution was refluxed for 8h. The reaction mixture was poured into water and extracted with DCM. 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 an alumina column using a mixture of (9:1) hexane and DCM. The yellow solid obtained upon the removal of solvent and it was recrystallized from a mixture (2:3) of DCM and methanol to separate pure **1d** (89%).



mp:- 122-124 °C.

IR ν_{max} (KBr):- 3040 (=C-H stretch), 2857 (-C-H stretch), 1350-1000 (C-N and C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$):- δ 7.43-8.48 (m, 9H), 4.44 (s, 2H), 3.63 (t, 4H, *J* = 4.8 Hz), 2.60 (t, 4H, *J* = 4.6 Hz).

^{13}C NMR ($CDCl_3$):- δ 131.43, 131.39, 129.06, 128.98, 127.58, 125.65, 125.00, 124.86, 67.13, 54.58, 53.68.

MS:- *m/z* 277 (M^+), 191.

Elemental analysis calculated for

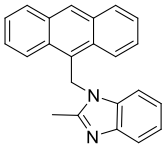
$C_{19}H_{19}NO$:- C: 82.28, H: 6.90, N: 5.05.

Found:- C: 82.29, H: 6.86, N: 5.02.

2.4.4.5. *N*-((Anthracen-9-yl)methyl)-2-methylbenzimidazole (1e).

2-Methyl benzimidazole (**3e**) (4.00 g, 30 mmol) was added to a solution of 9-chloromethylanthracene (**7**) (3.00 g, 15 mmol) in

15 mL dry benzene and stirred at RT under inert atmosphere for 24h. After the reaction was complete, reaction mixture was poured into water and extracted with diethyl ether to remove the side products. 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 recrystallized from a mixture of (1:4) hexane and dichloromethane to separate pure **1e** (79%).



mp:- 100-102 °C.

IR ν_{max} (KBr):- 3056 (=C-H stretch), 2850 (-C-H stretch), 1350-1000 (C-N and C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$):- δ 6.83-8.59 (m, 13H), 6.17 (s, 2H), 2.32 (s, 3H).

^{13}C NMR ($CDCl_3$):- δ 152.06, 142.55, 135.58, 131.31, 131.07, 129.63, 129.50, 127.31, 125.29, 124.66, 123.11, 122.14, 121.73, 119.08, 109.85, 42.02, 15.37.

MS:- *m/z* 323 (M+1), 191.

Elemental analysis calculated for

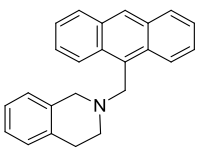
$C_{23}H_{18}N_2$:- C: 85.68, H: 5.63, N: 8.69.

Found:- C: 85.71, H: 5.67, N: 8.62.

2.4.4.6. *N*-((Anthracen-9-yl)methyl)-1,2,3,4-tetrahydroisoquinoline (1f).

Formic acid (1.00 mL, 27 mmol) was added to 1,2,3,4-tetrahydroisoquinoline (**1f**) (5.70 mL, 45 mmol) at RT and the mixture was rapidly cooled in an ice bath. When 9-anthraldehyde (**2**) (3.00 g, 15 mmol) was added to the reaction mixture and the

flask heated at 80 °C, rapid evolution of carbon dioxide was observed. After the evolution stopped the solution was refluxed for 8h. The reaction mixture was poured into water and extracted with DCM. The separated organic layer was washed with water and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the solid obtained was passed through an alumina column to remove charred materials using a mixture of (9:1) hexane and DCM. The yellow solid obtained upon the removal of solvent and it was recrystallized from a mixture (2:3) of DCM and ethyl acetate to separate pure **1f** (77%).



mp:- 128-130 °C.

IR ν_{max} (KBr):- 3053 (=C-H stretch), 2760 (-C-H stretch), 1350-1000 (C-N and C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$):- δ 6.95-8.53 (m, 13H), 4.61 (s, 2H), 3.85 (s, 2H), 2.78-2.91 (m, 4H).

^{13}C NMR ($CDCl_3$):- δ 135.19, 134.68, 131.51, 131.46, 129.71, 128.95, 128.64, 127.52, 126.60, 126.01, 125.68, 125.50, 125.16, 124.87, 56.22, 53.98, 50.49, 29.32.

MS:- *m/z* 323 (M^+), 191, 146.

Elemental analysis calculated for

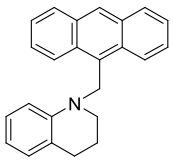
$C_{24}H_{21}N$:- C: 89.12, H: 6.54, N: 4.34.

Found:- C: 89.10, H: 6.55, N: 4.35.

2.4.4.7. *N*-((Anthracen-9-yl)methyl)-1,2,3,4-tetrahydroquinoline (1g).

Formic acid (1.00 mL, 27 mmol) was mixed with 1,2,3,4-tetrahydroquinoline (**3g**) (5.60 mL, 45 mmol) at RT and the

mixture rapidly cooled in an ice bath. When the mixture was heated at 80 °C after adding 9-anthraldehyde (**2**) (3.00 g, 15 mmol), rapid evolution of carbon dioxide was observed. After the evolution stopped, the solution was refluxed for 8h. The reaction mixture was poured into water and extracted with DCM. 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 an alumina column using a mixture of (9:1) hexane and DCM. Brown solid obtained (3.00 g) upon the removal of solvent was recrystallized from a mixture (2:3) of DCM and hexane to separate pure **1g** (64%).



mp:- 163-165 °C.

IR ν_{max} (KBr):- 3047 (=C-H stretch), 2770 (-C-H stretch), 1350-1000 (C-N and C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$):- δ 6.73-8.47 (m, 13H), 5.25 (s, 2H), 2.71-2.78 (m, 4H), 1.62-1.67 (m, 2H).

^{13}C NMR ($CDCl_3$):- δ 146.69, 131.59, 131.41, 129.27, 129.09, 128.48, 127.84, 127.27, 126.23, 125.08, 124.47, 123.89, 116.68, 110.66, 46.03, 44.83, 28.13, 22.54.

MS:- *m/z* 323 (M^+), 191, 132.

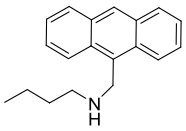
Elemental analysis calculated for

$C_{24}H_{21}N$:- C: 89.12, H: 6.54, N: 4.34.

Found:- C: 89.11, H: 6.55, N: 4.34.

2.4.4.8. 9-(*N,N*-Bisanthracenemethyl)butylamine (1h).

We employed Leuckart reaction for the synthesis of 9-(*N,N*-bisanthracenemethyl)butylamine (**1h**). To perform Leuckart reaction we initially synthesized the required secondary amine (*N*-butylaminomethyl)anthracene (**3h**) by modified Leuckart reaction.[47] Ammonium formate (0.95 g, 15 mmol) and *n*-butylamine (**4**) (1.5 mL, 15 mmol) were added to a solution of 9-anthraldehyde (**2**) (3.00 g, 15 mmol) in 40 mL dry benzene. This mixture was refluxed for half an hour, fitted with Dean-Stark apparatus to yield the corresponding imine. The reaction mixture was concentrated, dissolved in methanol and treated with a solution of $NaBH_4$ (1.10 g, 30 mmol) in methanol. After 3h the reaction mixture was concentrated, washed with water and the organic layer was separated using DCM followed by dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the obtained residue was passed through an alumina column using hexane as solvent. A yellow coloured fluorescent liquid which turned to solid **3h** (92%) while kept in freezer.



mp:- 38-40 °C.

IR ν_{max} (KBr):- 3421 (N-H stretch), 3054 (=C-H stretch), 2925 (-C-H stretch), 1448 (N-H bend), 1350-1000 (C-N and C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$):- δ 7.36-8.32 (m, 9H), 4.65 (s, 2H), 2.81 (t, 2H, *J* = 7.2 Hz), 1.47-1.52 (m, 2H), 1.26-1.35 (m, 2H), 1.18 (s, 1H), 0.85 (t, 3H, *J* = 7.4 Hz).

^{13}C NMR ($CDCl_3$):- δ 130.97, 130.58, 129.29, 128.13, 126.06, 125.02, 123.88, 123.16, 49.37, 44.88, 28.68, 19.54, 13.00.

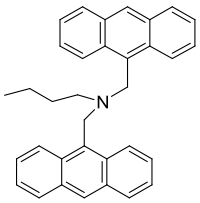
MS:- *m/z* 263 (M^+), 191.

Elemental analysis calculated for

$C_{19}H_{21}N$:- C: 86.65, H: 8.04, N: 5.31.

Found:- C: 86.64, H: 8.05, N: 5.31.

Formic acid (0.70 mL, 19 mmol) was mixed with (*N*-butylaminomethyl)anthracene (**3h**) (7.90 g, 30 mmol) at RT and the mixture was rapidly cooled in an ice bath. When the mixture was heated at 80 °C, after adding 9-anthraldehyde (**2**) (3.00 g, 15 mmol), rapid evolution of carbon dioxide was observed. After the evolution stopped, the solution was refluxed for 8h. The reaction mixture was poured into water and extracted with DCM. 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 using a mixture of (7:3) hexane and DCM. The yellow solid obtained upon the removal of solvent and it was recrystallized from a mixture (2:3) of DCM and hexane to separate pure **1h** (76%).



mp:- 186-188 °C.

IR ν_{max} (KBr):- 3085 (=C-H stretch), 2784 (-C-H stretch), 1350-1000 (C-N and C-C stretch) and 750-690 cm^{-1} (aromatic out of plane bending).

^{1}H NMR ($CDCl_3$):- δ 7.24-8.37 (m, 18H), 4.58 (s, 4H), 2.64 (t, 2H, *J* = 7.2 Hz), 1.64-1.71 (m, 2H), 0.97-1.07 (m, 2H), 0.60 (t, 3H, *J* = 8 Hz).

^{13}C NMR ($CDCl_3$):- δ 131.54, 131.38, 130.55, 128.84, 127.38, 125.37, 125.20, 124.70, 54.48, 50.80, 29.22, 20.60, 13.70.

MS:- *m/z* 191.

Elemental analysis calculated for

$C_{34}H_{31}N$:- C: 90.02, H: 6.89, N: 3.09.

Found:- C: 90.03, H: 6.89, N: 3.08.

2.5. References

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CHAPTER 3

EFFECT OF SOLVENT AND CONCENTRATION ON THE REACTIONS OF (ANTHRACEN-9-YL)METHANAMINES WITH SUITABLE DIENOPHILES

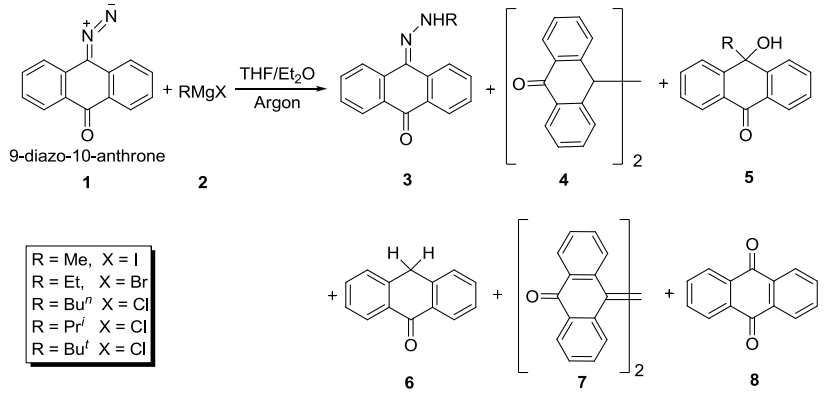
3.1. Abstract

Here we describe the reaction of (anthracen-9-yl)methanamines with different electron acceptors. These reactions exhibited dramatic solvent and concentration dependency. Depending on the solvent and concentration, reactions of (anthracen-9-yl)methanamines with different electron acceptors proceeded through one electron transfer, two electron transfer or Diels-Alder pathways and under certain conditions we observed multiple reaction pathways. We have proposed plausible mechanisms to account for various reactions observed by us.

3.2. Introduction

Competitive reactions are those in which a compound reacts simultaneously through more than one pathway to give different products. Several competitive reactions including one electron transfer versus nucleophilic attack[1-4] and unimolecular versus bim-

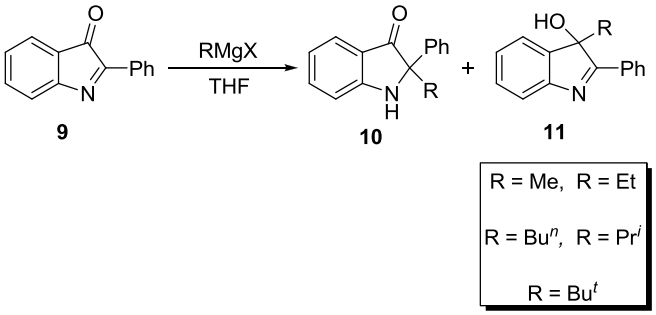
-olecular attacks are reported in literature.[5] A few photochemical[6] and gaseous phase reactions[7] also show competitive reactions. Reaction of 9-diazo-10-anthrone (**1**) with Grignard reagent **2** yielded different products as a result of competitive reactions including radical reaction and nucleophilic addition reaction. The ratio of the products formed by radical and nucleophilic pathway depends on the oxidation potential of the Grignard reagent[2] (Scheme **3.1**).



Scheme 3.1

In this reaction we can see different products formed simultaneously by different reaction pathways. Here products **4**, **6** and **7** are formed through a radical pathway and **3** is formed by the nucleophilic attack by Grignard reagent. Compound **5** is formed through the addition of Grignard reagents to **8** formed in the reaction medium or to the carbonyl group in the starting material **1** followed by hydrolysis during the reaction workup.

Grignard reagent reacts with 2-phenyl-3*H*-indol-3-one (**9**) to give 2,3-dihydro-2-alkyl(or phenyl)-2-phenylindol-3-ones **10** and 2-phenyl-3-alkyl(or phenyl)-3H-indol-3-ols **11**. Here also, the ratio of the two products depends on the Grignard reagent used[1] (Scheme **3.2**).



Scheme 3.2

Here products **10** and **11** are formed by the radical mediated pathway and nucleophilic attack respectively. Mechanism of the reaction gives an idea about the products which are formed by the competitive reaction between radical mediated pathway and nucleophilic attack.

In this chapter, we summarize the reaction of (anthracen-9-yl)methanamines[8,9] with different dienophiles. The structures of (anthracen-9-yl)methanamines (**12a-h**) and dienophiles (**13a-c**) employed in this investigation is given in Chart **3.1**.

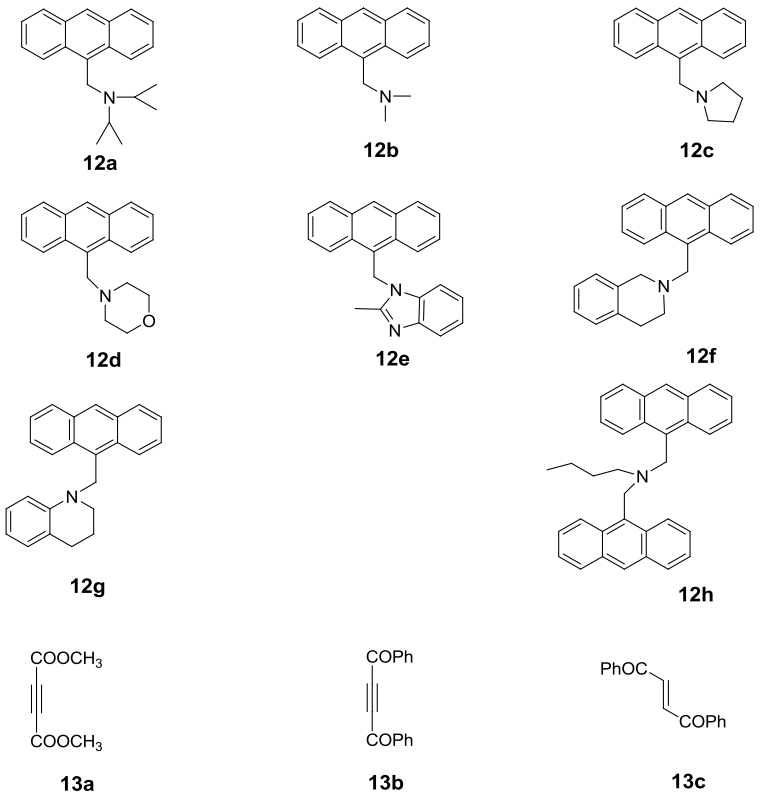


Chart 3.1

Close examination of the structural features of the substrates suggests that single electron transfer, Michael addition and Diels-Alder reaction possibilities exist here. Thus, reaction between anthracenemethanamines and suitable dienophiles also come under the class of competing reactions. It may be noted that single electron transfer, Michael addition and Diels-Alder reaction between anthracenemethanamines and dienophiles are bimolecular reactions and hence are strongly influenced by concentration. Based on literature precedents, it is clear that the transition state for single electron transfer reactions are loosely bound whereas Diels-

Alder reaction requires tighter and better aligned transition state to proceed smoothly. On the other hand, a polar transition state is involved in Michael additions. Such polar transition states are stabilized by polar protic solvents. Thus it may be expected that single electron transfer reactions take precedence over Michael addition and Diels-Alder reactions in nonpolar media under dilute conditions. At higher concentrations, Diels-Alder reaction will be competitive provided a sufficiently high boiling solvent is employed. Michael addition is competitive in polar protic solvents. These considerations provided us challenging opportunities to examine competing reactions of anthracenemethanamines with electron deficient dienopohiles as a function of several variables including solvent polarity, nature of the solvent, nature of substrates, reaction temperature and concentration. Successful completion of our investigation was contingent upon availability of starting materials that exhibit good solubility in different types of organic solvents. In addition, both starting materials and products should exhibit low polarity to enable separation from tarry materials that are likely to be generated under the reaction conditions due to polymerization of dienophile component and degradation of amine components to polar fractions. Based on these considerations, we adopted 9-(*N*,*N*-diisopropylaminomethyl)anthracene (**12a**) as the primary substrate for our investigations.

3.3. Results and Discussion

We have selected reaction between (anthracen-9-yl)methanamines and suitable electron deficient dienophiles for studying the solvent and concentration dependency because one electron transfer, two electron transfer and Diels-Alder reaction possibilities exist between these versatile substrates. In other words we can examine competition between three types of reactions in a single system. For studying the solvent dependency (and temperature dependency where applicable), we have selected nonpolar solvent – xylene, polar aprotic solvents – DMF and acetonitrile, and polar protic solvents – alcohol (methanol) and acid (acetic acid). At lower concentrations, in both nonpolar and polar aprotic solvents, the reaction proceeded through one electron transfer pathway. But in polar protic solvents, reaction occurred through both one electron and two electron transfer pathways. We could observe competition between one electron and two electron transfer reactions under lower concentration of (anthracen-9-yl)methanamines.

We repeated the reaction of (anthracen-9-yl)methanamines with dienophiles with a tenfold increase in concentration of the substrates in different solvents. In nonpolar and polar aprotic solvents, the major radical pathway is shifted to Diels-Alder pathway. In polar protic solvent, acetic acid - the reaction proceeds through one electron transfer, two electron transfer and Diels-Alder reactions. We could not examine the effect of concentration in

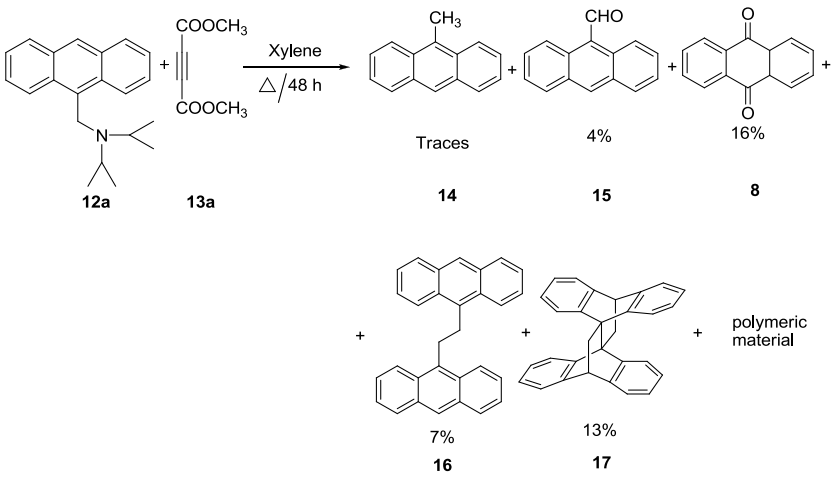
methanol reactions because of low solubility of (anthracen-9-yl)methanamines in this solvent. Furthermore, Diels-Alder reaction is an unlikely competing pathway in low boiling point solvents such as methanol.

At higher concentration, in nonpolar and polar aprotic solvents we observed competition between one electron transfer and Diels-Alder pathways. Here the Diels-Alder pathway is the major one. But in polar protic solvent - acetic acid, we observed competition between one electron transfer, two electron transfer and Diels-Alder reactions. Here two electron transfer and Diels-Alder reaction are the major pathways. In continuation we have also examined the nature and reactivity of dienophiles like dimethyl acetylenedicarboxylate (DMAD), dibenzoylacetylene[10] (DBA) and dibenzoylethylene[11] (DBE). With each of these dienophiles, reactions proceeded through same mechanism in each solvent. Reactivity of acetylenes depends on the substituents attached. It may be stated here that electron transfer reactions of (anthracen-9-yl)methanamines with an inorganic oxidant - ceric ammonium nitrate (CAN) - was already established by our research group.[12] The observations and proposed mechanisms for reactions under various conditions are discussed below:-

3.3.1. Reactions of (Anthracen-9-yl)methanamines with suitable dienophiles in different solvents at different concentrations

3.3.1.1. Reactions in non-polar solvent:- xylene

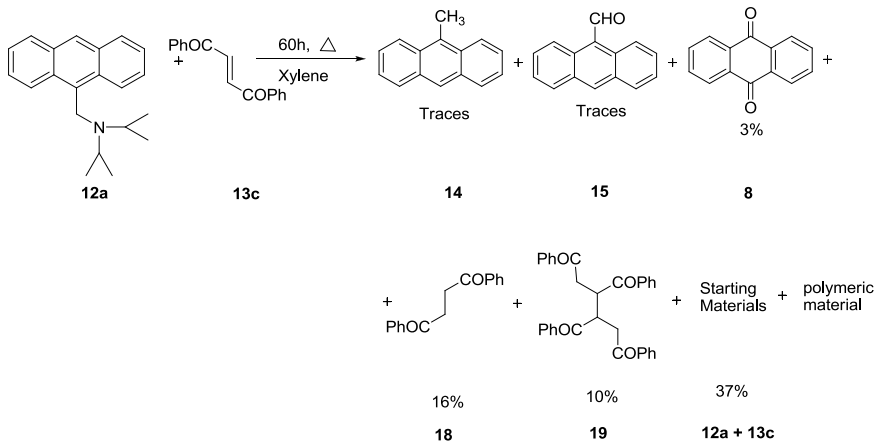
A 0.034 M solution of 9-(*N*,*N*-diisopropylaminomethyl)anthracene (**12a**) was refluxed with 4 equivalents of DMAD (**13a**) in xylene. After 48h, the starting material **12a** was completely consumed to give a variety of products including 9-methylanthracene (**14**), 9-anthraldehyde (**15**), 9,10-anthraquinone (**8**), 1,2-bis(9-anthracenyl)ethane[9,13,14] (**16**) and lepidopterene (tetrabenzotetracyclotetradecatetraene) (**17**)[9,15-18] in moderate yields. The reaction was accompanied by high degree of DMAD polymerisation due to electron transfer reaction (Scheme **3.3**).



Scheme 3.3

To assess the effect of nature and reactivity of dienophiles, we repeated the above reaction with DBA and DBE. We have employed the same condition for DBA reaction as with the DMAD reaction, for studying the effect of dienophile in dilute condition. Here the same products depicted in Scheme **3.3** were formed albeit in slightly different yields and the reaction was completed in 42h. We did not observe any significant difference in the DBA reaction with respect to DMAD reaction.

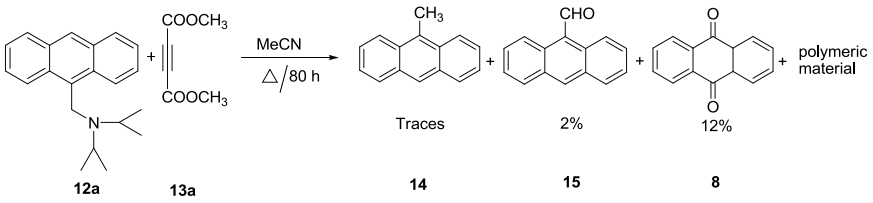
In continuation, we examined the reaction of 9-(*N*,*N*-diisopropylaminomethyl)anthracene (**12a**) with DBE. Electron deficiency of DBE is comparatively low in comparison with DMAD and DBA. Due to lower reactivity of DBE, its reaction with **1a** is very slow when compared to DMAD and DBA reactions. After 60h, in addition to unreacted starting materials, 9-methylanthracene (**14**), 9-anthraldehyde (**15**), 9,10-anthraquinone (**8**), dibenzoyl ethane[19,20] (**18**) and 1,6-diphenyl-3,4-dibenzoyl-l,6-butanedione[21,22] (**19**) are obtained (Scheme **3.4**). Interestingly, here the dimers **16** and **17** were not formed in detectable amounts.



Scheme 3.4

3.3.1.2. Reactions in polar aprotic solvents:- Acetonitrile and Dimethylformamide

We were interested in unravelling the outcome of the reaction in polar aprotic or non-nucleophilic polar solvents such as dimethylformamide (DMF) and acetonitrile. By selecting these two solvents we could also examine the effect of temperature on the reaction. We refluxed a 0.034 M solution of **12a** with 4 equivalents of DMAD in DMF. The reaction was completed in 35h. The products obtained were same as depicted in Scheme **3.3** but in different yields. We have also carried out the reaction in acetonitrile, to study the effect of temperature. After 80h the starting materials were completely reacted to give the same products except **16** and **17** along with some polymerized material (Scheme **3.5**).



Scheme 3.5

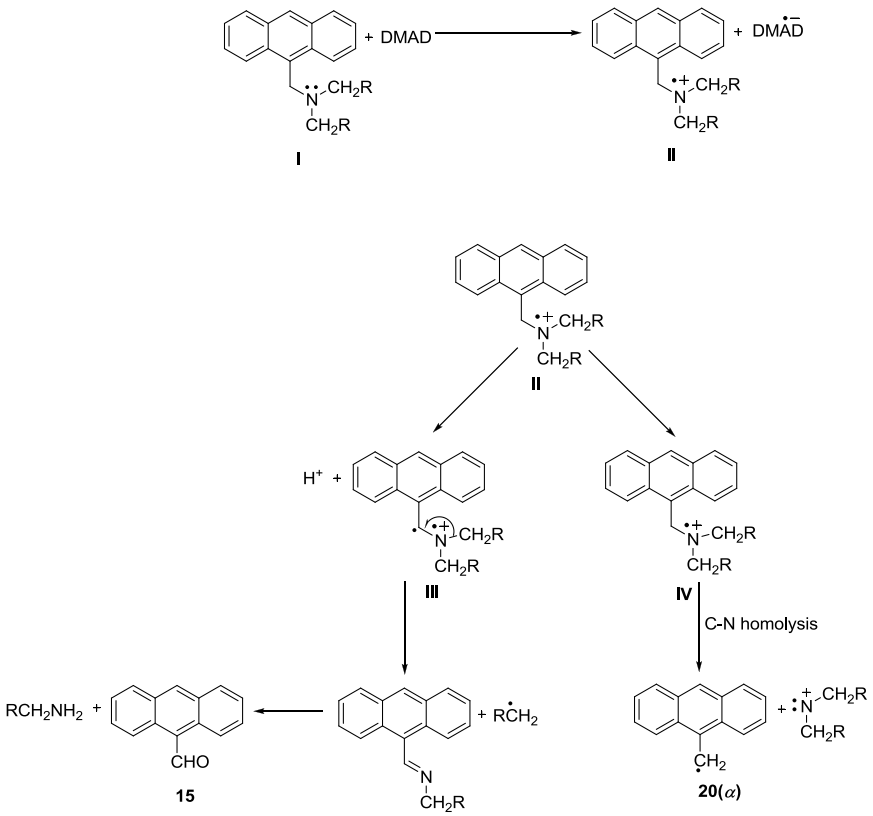
To study the effect of nature and reactivity of dienophiles, we carried out the reaction of 0.034 M solution of **12a** with 4 equivalents of DBA and DBE. These reactions also gave the same products in different yields as in the reaction in xylene. Based on these results, we concluded that the reaction proceeded through the same mechanism in both non-polar and polar aprotic solvents.

All products were completely characterized on the basis of spectral and analytical data, where applicable by comparison with authentic samples prepared through reported procedures. Formation of 9-methylanthracene (**14**), for example, was confirmed by TLC, ^{1}H NMR and MS data. Similarly, formation of 9-anthraldehyde (**15**), 9,10-anthraquinone (**8**), 1,2-bis(9-anthracenyl)ethane (**16**) and lepidopterene (**17**) are confirmed by IR, ^{1}H NMR, ^{13}C NMR and MS data.

A close like at the product distribution suggests involvement of multiple reaction pathways. Anthraquinone (**8**) is probably generated through the involvement of adventitious oxygen. We propose direct reaction of triplet oxygen with 9-(*N*,*N*-diisopropylaminomethyl)anthracene (**12a**) for the generation of 9,10-anthraquinone (**8**). According to Kuroda *et al.* 9,10-bis(1-

hydroxyalkyl)anthracenes are converted to their respective endoperoxides with the reaction of triplet oxygen.[23] They showed that endoperoxide formation is assisted by the lone pair electron of oxygen in the side chain of the anthracene ring. In our case the (anthracen-9-yl)methanamines **12a-h** contain nitrogen having available electron pair in the side chain of anthracene ring and hence endoperoxide generation by reaction with triplet oxygen is feasible here as well. Formation of endoperoxide followed by homolysis and β-scission lead to the generation of 9,10-anthraquinone (**8**). Anthraldehyde (**15**), on the other hand is generated through electron transfer mediated pathway followed by β-hydrogen loss to give imine precursor that undergoes hydrolysis under workup conditions to yield the aldehyde product. Similarly, 9-methylanthracene (**14**) is also generated through electron transfer pathway. Products such as 1,2-bis(9-anthracenyl)ethane (**16**) and lepidopterene (**17**) are isomeric in nature, sharing the molecular formula $C_{30}H_{22}$. We propose that 9-methylanthracene (**14**), 9-anthraldehyde (**15**), 1,2-bis(9-anthracenyl)ethane (**16**) and lepidopterene (**17**) are formed from a common intermediate: amine radical cation generated through single electron transfer to the dienophile. Subsequent C-N bond homolysis leads to the generation of anthracenemethyl radical and nitrenium ion intermediates whereas β-hydrogen atom loss followed by bond reorganization leads to the generation of imine precursor of anthraldehyde. Preferential cleavage of C-N bond in the 9-anthracenemethyl side over other α-methyl groups may be due to

the higher stability of 9-anthracenemethyl radical. The general mechanism[24-27] for the formation of 9-anthracenemethyl radical and 9-anthraldehyde (**15**) is presented in Scheme **3.6**.



Scheme 3.6

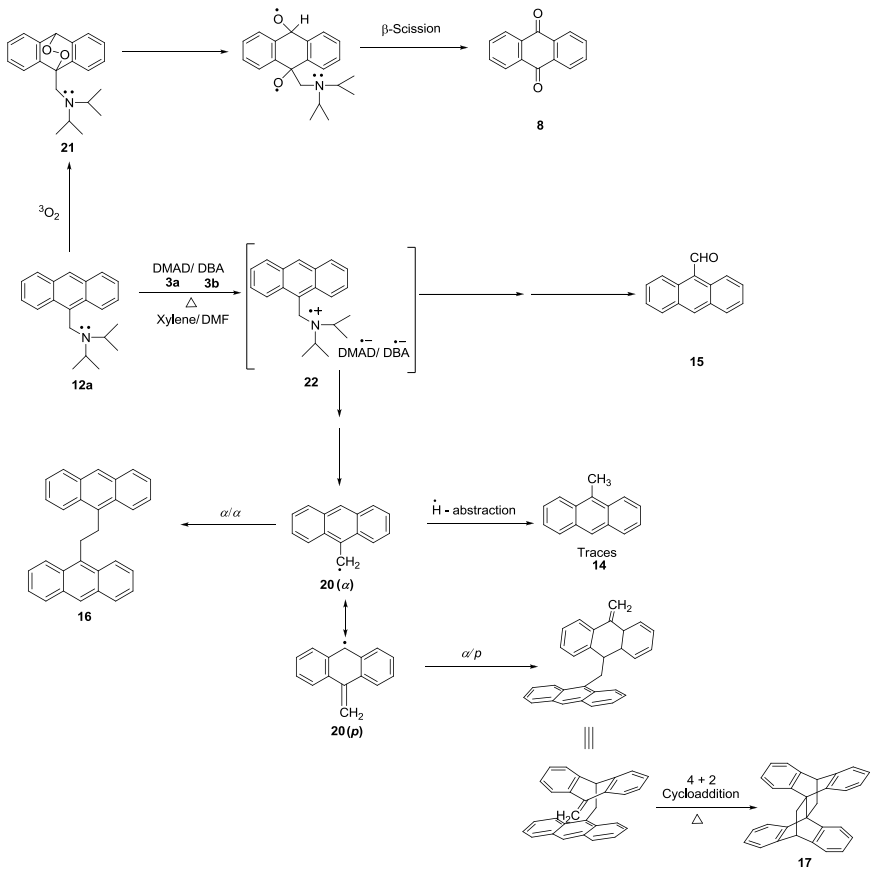
Isomers **16** and **17** are formed by the dimerization of 9-anthracenemethyl radical **21** which in turn is a clear indicator to involvement of radical pathway in the reaction. Hydrogen atom abstraction by 9-anthracenemethyl radical **20**(α) leads to the formation of 9-methylanthracene (**14**). Here we observe two

competing reactions: 1) dimerization and hydrogen radical abstraction by 9-anthracenemethyl radical, 2) regioselectivity in dimerization step. From the above results we conclude that dimerization pathway predominates over hydrogen radical abstraction pathway.[9] Additionally, 9-anthracenemethyl radical can be viewed as a hybrid of **20**(***α***) and **20**(***β***) forms. Simple α/α dimerization leads to the formation of **16** and α/p dimerization followed by intramolecular [4+2] Diels-Alder cycloaddition results in the generation of **17**[28] (Scheme **3.7**). Austin Model 1 calculation[29] explained the preferential formation of **17** over **16** because the ground state of the 9-anthracenemethyl radical has three fold higher spin density in the *p* position than in the α position, which facilitates the α/p attack to form **17**. However, under conditions where anthracenmethyl radical is generated in very low concentration, dimerization is suppressed.

In order to confirm the involvement of dienophiles in the generation of various products, we carried out a control experiment by refluxing a solution of **12a** in xylene in the absence of dienophiles. After prolonged reflux, unchanged **12a** was recovered in near-quantitative amounts. This result clearly indicates the role of dienophiles in the reaction.

Anthraquinone (**8**) is formed through the intermediate endoperoxide **21** by the direct reaction of **12a** with triplet oxygen followed by the β-scission.[30] Generally endoperoxides are generated by the reaction with singlet oxygen, but a handful of literature references[23,31] show the formation of endoperoxide by the

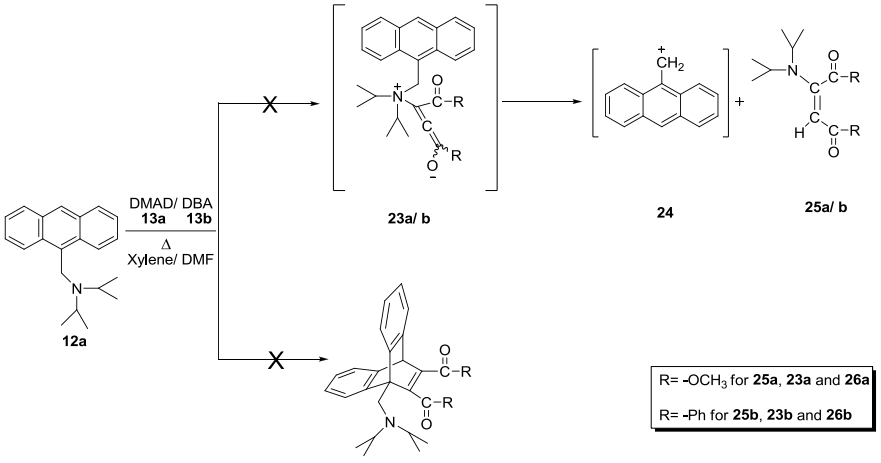
reaction with triplet oxygen.



Scheme 3.7

Along with one electron transfer reaction, we explored incidence of competing reactions like Diels-Alder reaction or Michael type addition of **12a** with dienophiles **13a** and **13b**. Michael addition of anthracenemethanamines to dienophiles leads to the formation of zwitterion **23a/23b** followed by C-N bond heterolysis to form 9-anthracenemethyl cation (**24**) and the

corresponding *N*,*N*-diisopropylaminomethylmaleate/fumarate (**25a**) or 2-diisopropylaminodibenzoylethylene (**25b**) respectively (Scheme **3.8**). We carried out a careful GC-MS analysis to search for the generation of Diels-Alder adduct **26a/26b**, *N*,*N*-diisopropylaminomethylmaleate (**25a**), 2-diisopropylaminodibenz-oylethylene (**25b**) and any nitrogen containing fragment formed during the above reactions (Scheme **3.8**). But the GC-MS result did not give any indication of above three possibilities ruling our neucleophilic addition possibilities.

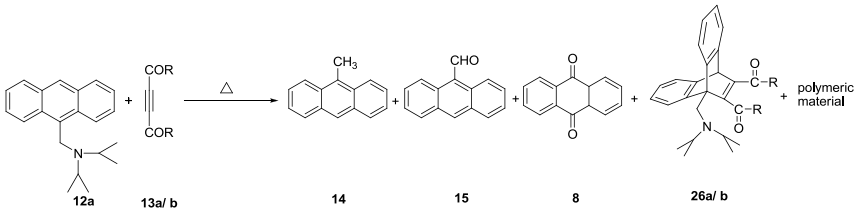


Scheme 3.8

With a view to determine the generality of the reaction, we have examined the reaction of several (anthracen-9-yl)methanamines **12b-e** with dienophiles **13a-b** (Chart **3.1**) in refluxing xylene and DMF. In these amines, we have carefully modulated the electronic and steric environment around the

significant nitrogen atom. In all these cases, the results are analogous with those obtained in the reaction between **12a** and **13a-b**. Here also we could not locate the amine component formed during the reaction. This led to the conclusion that extensive degradation of the amine component takes place probably through subsequent electron transfer pathways to give volatile lower primary or secondary amines or even ammonia, which are lost during the reaction or work up of the product mixture. This suggestion is based on the observation that upon completion of the reaction, the reaction mixture had a noticeable ammoniacal odour. Such degradation reactions have literature precedence.[24-27,32,33]

As mentioned earlier, we assumed that at higher concentrations, bimolecular reactions involving tighter transition states will be competitive with electron transfer reactions. To check this assumption, we refluxed a 0.34 M solution of **12a** with three equivalents of **13a** or **13b** in nonpolar solvent, xylene and polar aprotic solvent, DMF (Scheme **3.9**). Reaction time depended on the solvent and dienophile used in the reaction. Comparison of experimental results of low concentration and high concentration reactions provided insightful results. Products such as **14**, **15** and **8** are common in both the reactions. While **16** and **17** were generated under dilute conditions, these were totally absent in reactions carried out under higher concentration. As expected, Diels-Alder adduct **26a/b** was generated in appreciable amounts in reactions carried out under higher concentrations.



R = -OCH_3 for **13a** then,
In xylene:- 25 h
14, **15** and **8** = Traces, **26a** = 64%
In DMF:- 20 h
14, **15** and **8** = Traces, **26a** = 58%

R = -Ph for **13b** then,
In xylene:- 23 h
14, **15** and **8** = Traces, **26b** = 66%
In DMF:- 20 h
14, **15** and **8** = Traces, **26b** = 64%

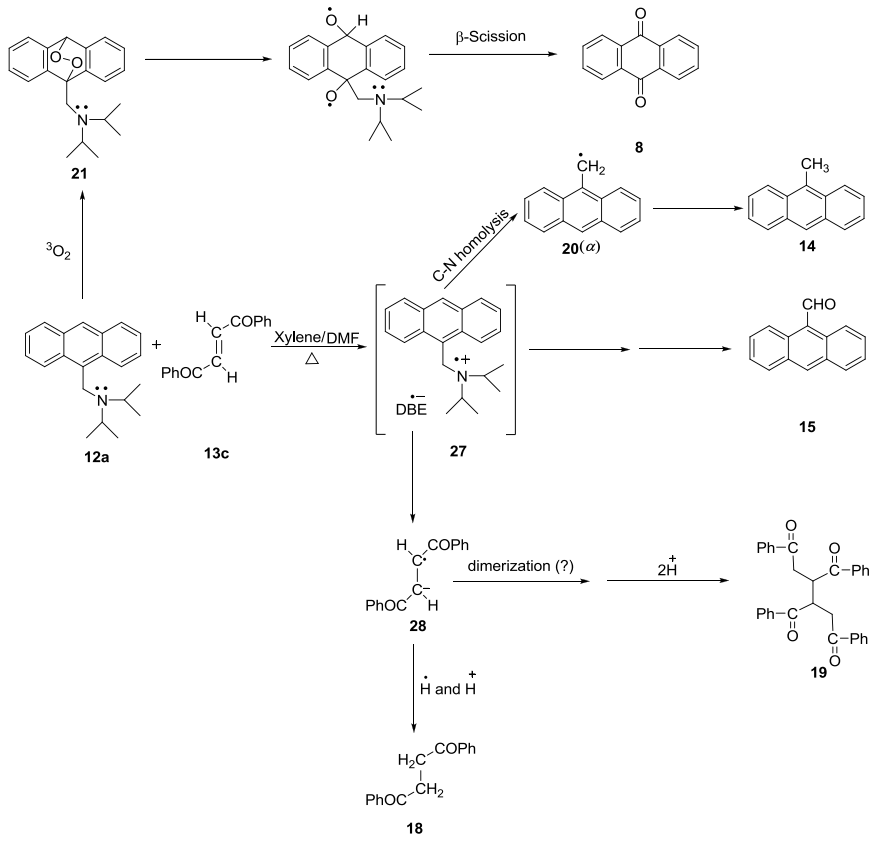
Scheme 3.9

When the concentration of the reactant increased tenfold, the major pathway is the Diels-Alder pathway and the minor is one electron transfer pathway. Under higher concentrations, we could not detect **16** and **17** indicating that 9-anthracenemethyl radical formed through a single electron transfer pathway (*vide supra*) is generated in very low concentration where dimerization possibility is non-existent. In other words, in this reaction involving competing reaction sequences, Diels-Alder pathway is far more prominent than single electron transfer reaction under higher concentrations.

Based on the above results, we conclude that at lower concentration of **12a** in nonpolar and polar aprotic solvents one electron transfer reaction is predominant. When the concentration of **12a** increased tenfold, preference was shifted to Diels-Alder pathway. Interestingly, we can alter the major reaction pathway by changing reaction conditions.

Reactivity of DBE is much lower in comparison with DBA

and DMAD and this is truly reflected in reactions carried out by us. The proposed mechanism for DBE reaction is same as that for the DMAD and DBA reactions in which one electron transfer occurs from **12a** to DBE (**13c)** thereby forming a radical anion radical cation pair **27**. Compounds **14**, **15** and **8** are formed by the same mechanism as shown in Scheme **3.6**. Actual mechanism of formation of **18** and **19** remains speculative. These may be formed through the intermediate DBE radical anion **28**. Abstraction of hydrogen atom and a proton by **28** may yield the reduced product dibenzoylethane (**18**). Radical dimerization[21] of two DBE radical anions followed by abstraction of two protons generates 1,6-diphenyl-3,4-dibenzoyl-l,6-butanedione (**19**) (Scheme **3.10**). Since the reactivity of DBE is very low, about 40% of starting materials was recovered from the reaction mixture after 60h.

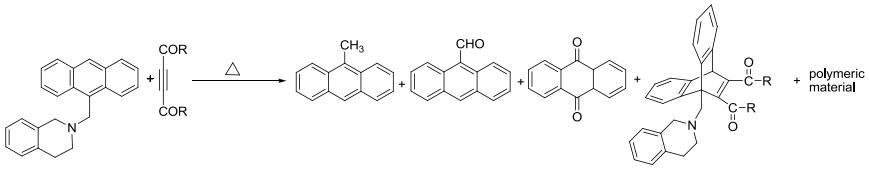


Scheme 3.10

In order to reveal the fate of amine fragment in reactions done at low concentration, we examined the reaction of higher amine appended (anthracen-9-yl)methanamines **12f-h** shown in Chart **3.1** with dienophiles **13a** and **13b**. When a 0.031 M solution of **1f** with four equivalents of **13a/b** in xylene and DMF, products identical to those presented in Scheme **3.3** were generated, but in different yields. From this reaction also we could not get any information on amine component.

In continuation, with a view to understand the effect of con-

-centration, a 0.16 M solution of *N*-((anthracen-9-yl)methyl)-1,2,3,4-tetrahydroisoquinoline (**12f**) in xylene was refluxed with three equivalents of DMAD. Products **14**, **15**, **8** and **29a** were generated under these conditions. As expected, the oxidised product **15** and one electron transfer mediated products **14**, **15** were formed in very low yield. Though GC-MS analysis of the reaction mixture indicated that the major product formed in the reaction is **29a**, the Diels-Alder adduct, we could not separate this adduct in pure form. Though we employed different conditions for the separation of pure adduct, it remained inseparable from polar materials generated in this reaction. In continuation, we examined the reaction of **12f** with DMAD in DMF. Products identical to those obtained in the xylene reaction were formed under these conditions as well. Reaction of **12f** in both xylene and DMF with DBA also gave products similar to those obtained with DMAD (Scheme **3.11**).



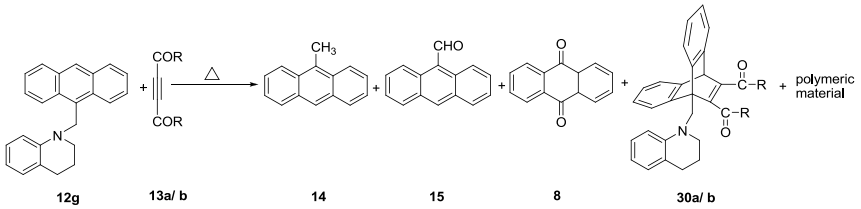
12f 13a/ b 14 15 8 29a/ b (couldn't purify)

R = -OCH_3 for **13a** then,
In xylene:- 12 h
14 = Traces, **15** = 2%, **8** = 7% and **29a** = 40%
In DMF:- 10 h
14 = Traces, **15** = 2%, **8** = 8% and **29a** = 45%

R = -Ph for **13b** then,
In xylene:- 18 h
14 = Traces, **15** = 2%, **8** = 10% and **29b** = 50%
In DMF:- 20 h
14 = Traces, **15** = 3%, **8** = 12% and **29b** = 48%

Scheme 3.11

We reasoned that lowering electron density around nitrogen atom will reduce electron transfer possibility. This is easily achieved by delocalizing lone pair electrons available on nitrogen. In order to test this hypothesis, we examined the reaction of *N*-((anthracen-9-yl)methyl)-1,2,3,4-tetrahydroquinoline (**12g**) with dienophiles **13a** and **13b** in both xylene and DMF by applying the same conditions as with **12f** (Scheme **3.12**). The reaction pathways are same as that in the reaction of **12f** with the major difference that products arising through single electron transfer possibility are generated in insignificant amounts. The major pathway in this reaction is the Diels-Alder pathway.



12g 13a/ b 14 15 8 30a/ b

R = -OCH_3 for **13a** then,
In xylene:- 36 h
14, **15** = Traces, **8** = 2% and **30a** = 58%
In DMF:- 40 h
14, **15** = Traces, **8** = 3% and **30a** = 55%

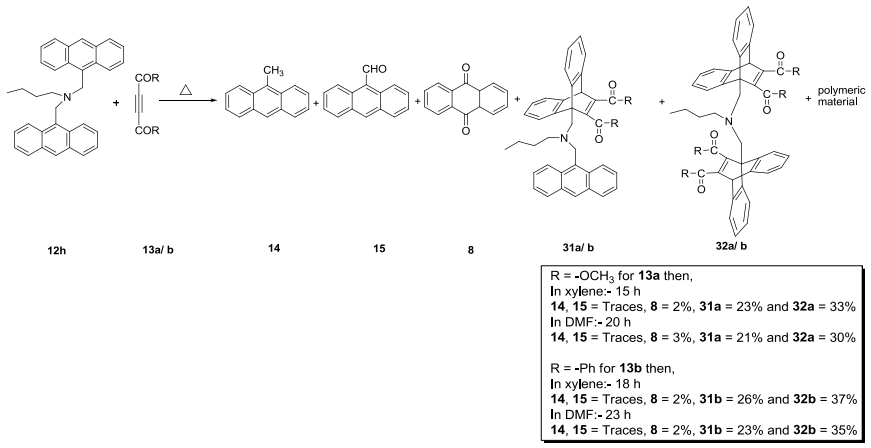
R = -Ph for **13b** then,
In xylene:- 38 h
14, **15** = Traces, **8** = 3% and **30b** = 60%
In DMF:- 31 h
14, **15** = Traces, **8** = 3% and **30b** = 58%

Scheme 3.12

From our experience, electron transfer reaction is favoured under lower concentration of (anthracen-9-yl)methanamines. So we carried out the reaction of **12g** in 0.031 M concentration in both xylene and DMF. But in this case, the reaction was slow and

proceeds through Diels-Alder pathway due to the less availability of electrons. For studying the radical reaction we have again diluted the reaction mixture to 0.015 M concentration. In this case the reactions in xylene and DMF are very slow and unchanged **12g** was recovered in significant amounts along with some polymerized products.

Though we repeated the experiments several times by changing concentration, reaction time and temperature, we could not isolate any nitrogen containing products from **12a-g**. This is probably due to degradation of nitrogen containing fragments to small molecules that evaded detection and isolation. We envisioned that incorporating bulky substituents on to nitrogen may result in fragments that are isolable or at least detectable by GC-MS. In order to unravel the fate of the nitrogen containing fragment in the reactions of (anthracen-9-yl)methanamines with dienophiles **13a** and **13b** in both xylene and DMF, we selected 9-(*N*,*N*-bisanthracenemethyl)butylamine (**12h**). Refluxing 0.11 M solution of 9-(*N*,*N*-bisanthracenemethyl)butylamine (**12h**) in both xylene and DMF with three equivalents of dienophiles **13a** yielded **14**, **15**, **8**, **31a** and **32a** (Scheme **3.13**). In this reaction also the major pathway is Diels-Alder pathway and the minor one is radical pathway. Here we can see the competition reaction between radical mediated pathway and Diels-Alder pathway. As in the above reactions Diels-Alder pathway is the major pathway.



Scheme 3.13

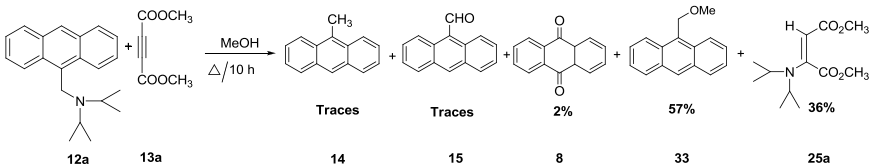
In order to bias the reaction towards single electron transfer mediated path, we repeated the reaction at reduced concentration. A 0.031 M solution of **12h** was treated with dienophile in both xylene and DMF. The reaction in each solvent was slow and proceeded through Diels-Alder pathway. We reduced the concentration to 0.011 M to study the one electron transfer reaction and check the possibility for Hofmann-Loffler-Freytag reaction. But we could not isolate any products, unchanged **12h** was recovered in substantial amounts. Apparently, steric congestion around nitrogen resulted in substantial decrease in single electron transfer and hence our goal of unraveling the fate of nitrogen containing fragments remains unaccomplished.

In summary, we observed that, at low concentrations, single electron transfer mediated processes predominate in the reaction between anthracenemethanamines and electron deficient dienophiles in both nonpolar and polar aprotic solvents. In contrast,

Diels Alder reaction is the major reaction pathway when the reactions are carried out at higher concentrations in both types of solvents. Steric crowding around nitrogen can possibly impair single electron transfer pathway.

3.3.1.3. Reactions in polar protic medium:- Alcohol, Methanol

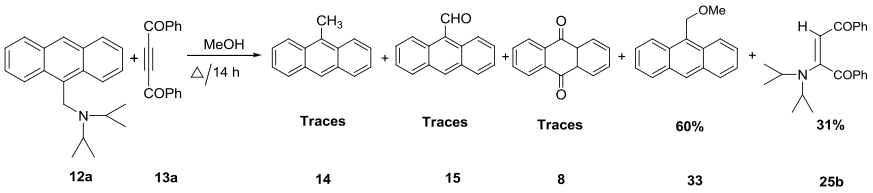
As stated earlier, we reasoned that reactions involving polar transition states will be more competitive in polar protic solvents. With a view to test this hypothesis, we examined the reaction of **12a** with dienophiles in polar protic solvents. We selected methanol (highly polar, but low boiling) and acetic acid (intermediate polarity and boiling point) for this investigation. When a solution of **1a** in methanol was refluxed with 1.5 equivalents of DMAD for 10h, 9-(methoxymethyl)anthracene (**33**) and methyl *N*,*N*-diisopropylaminomaleate (**25a**) were formed in good yields along with **14**, **15** and **8** in negligible amounts (Scheme **3**.**14**).



Scheme 3.14

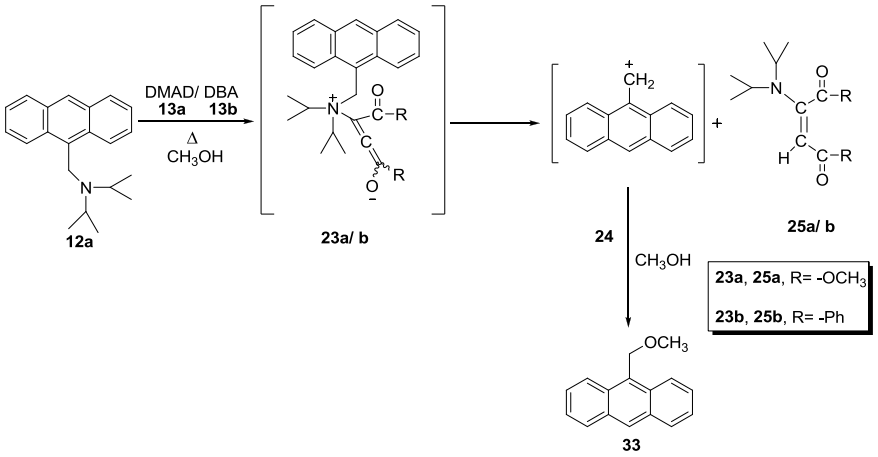
To study the effect of dienophiles in reaction carried out in methanol, we repeated the reaction of **12a** with **13b** and **13c**. Reaction with **13b** was completed in 14h and the products obtained

are similar to those depicted in Scheme **3.14**. Major products obtained are 9-(methoxymethyl)anthracene (**33**) and 2-diisopropylaminodibenzoylethylene (**25b**) with trace amounts of **14**, **15** and **8** (Scheme **3.15**).



Scheme 3.15

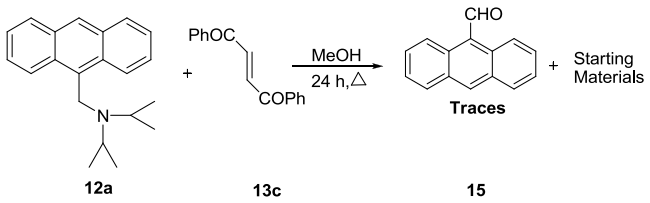
We propose that the above reactions take place through the nucleophilic attack of amine on dienophiles (**13a** and **13b**) in a Michael type addition pathway giving rise to a Michael adduct/ zwitterion[37] **23a/b** (Scheme **3.16**). This leads to the weakening and eventual cleavage of C-N bond giving rise to 9-anthracenemethyl cation (**24)** and **25a** or **25b**. 9-Anthracenemethyl cation (**24**) formed is captured by the solvent to give the corresponding ether **33**. Solvent assisted SN2 reactions also lead to the formation of these products. But we favour SN1 mechanism in this case due to steric factors and polar protic nature of the solvent.[38]



Scheme 3.16

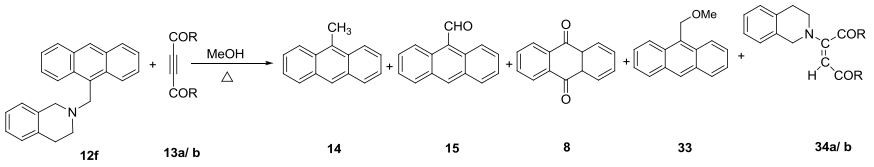
Minor products such as **14**, **15** and **8** are formed by the mechanism explained in Scheme **3.7**. In these reactions, we observed competition between one electron transfer and two electron transfer reactions. From experimental results, we concluded that two electron transfer reaction is the major pathway.

Reactivity of **13c** is considerably lower and hence the reaction between **12a** and **13c** proceeded very slowly. After 24h, we could detect trace amounts of **15** as the only product formed. Unchanged starting materials were isolated in near-quantitative amounts (Scheme **3.17**). Other (anthracen-9-yl)methanamines **12b-f** reacted in the same way with dienophiles in methanol.



Scheme 3.17

It should be mentioned here that (anthracen-9-yl)methanamines **12a-f** have very low solubility in methanol. So we dissolved **12a-f** in minimum amount of dichloromethane and the solution was diluted with excess methanol and this mixture was refluxed with appropriate dienophile. (Anthracen-9-yl)methanamine having significant amine component **12f** reacted in the same way as that of **12a-e** (Scheme **3.18**).



R = -OCH_3 for **13a** then,
Time:- 10 h
14, **15** = Traces, **8** = 3%, **33** = 46% and **34a** = 36%

R = -Ph for **13b** then,
Time:- 16 h
14, **15** = Traces, **8** = 4%, **33** = 48% and **34b** = 31%

Scheme 3.18

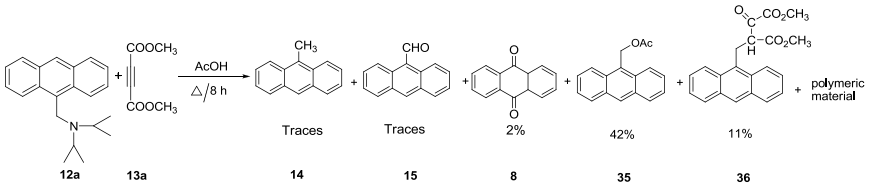
(Anthracen-9-yl)methanamines **12g** and **12h** are insoluble in methanol. When methanol was added to a solution of **12g,h** in dichloromethane, the compound precipitated out immediately. So we could not examine the reaction of **12g**,**h** with dienophiles in methanol.

Our research group has already established that the rate of the reactions in alcohol media depends up on the boiling point of the alcohol used.[39] The reaction was faster in higher boiling alcohols such as ethanol, allyl alcohol, 1-propanol, *t*-butanol and 1-butanol. All the above reactions proceed through the same pathway indicated in Scheme **3.16** and we conclude that the alcohol reactions occur through major ionic pathway giving rise to products arising through 9-anthracenemethyl cation (**24**) intermediate. During the course of the alcohol reactions with **13a** and **13b**, we observed the competition reaction between one electron transfer and two electron transfer mediated reactions. Here the two electron transfer reaction is the major pathway. Due to the relatively low boiling pint of the alcohol solvents and the higher propensity for anthracenemethanamines to undergo Michael type addition, Diels-Alder reaction was not observed in any of the cases examined by us. The natural question here is: if nucleophilicity of amines is reduced by protonation, will Diels-Alder reaction become competitive? In order to answer this question, we devised the following set of experiments.

3.3.1.4. Reactions in polar protic medium:- Acid, Acetic Acid

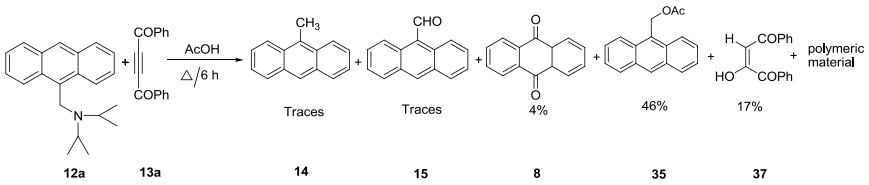
Generally amines get protonated by acids. With this assumption we carried out the reaction of **12a** with dienophiles **13a**, **13b** and **13c** in glacial acetic acid. We reasoned that

protonation will reduce the electron transfer reaction in the dilute condition and the reaction may occur through some other competing pathway. To check this possibility we refluxed 0.034 M solution of **12a** with 2 equivalents of **13a** in glacial acetic acid, but the result of the reaction was surprising. After 8h, we obtained (anthracen-9-yl)methyl acetate[40-42] (**35**) and 2-(anthracen-9-ylmethyl)dimethyl-3-oxosuccinate (**36**) along with trace amounts of **14**, **15** and **8** (Scheme **3.19**). It may be noted here that **25a** was not present in detectable amounts in the reaction mixture.



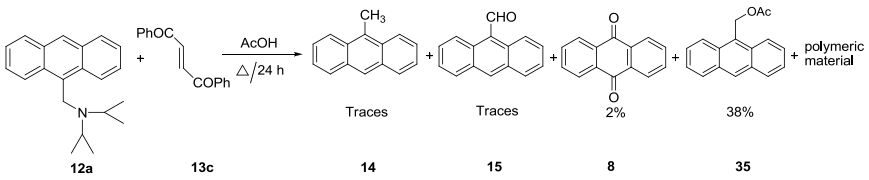
Scheme 3.19

For studying the effect of dienophiles in the above reaction, we repeated the reaction of **12a** with dienophiles **13b** and **13c**. Reaction of 0.034 M solution of **12a** with 2 equivalents of **13b** was completed in 6h yielding 2-hydroxydibenzoylethylene[43,44] (**37**) instead of **36** (Scheme **3.20**) along with other products depicted in Scheme **3.19**. As with DMAD reaction, **25b** could not be detected in the product mixture in this case as well.



Scheme 3.20

In continuation of the study on the effect of dienophiles, we repeated the reaction of **12a** with **13c** in glacial acetic acid. Here we slightly increased the concentration of **12a** because **13c** has low reactivity compared to other dienophiles used. Refluxing 0.048 M solution of **12a** with 2 equivalents of **13c** in glacial acetic acid yielded **14**, **15**, **8** and **35** (Scheme **3.21**).

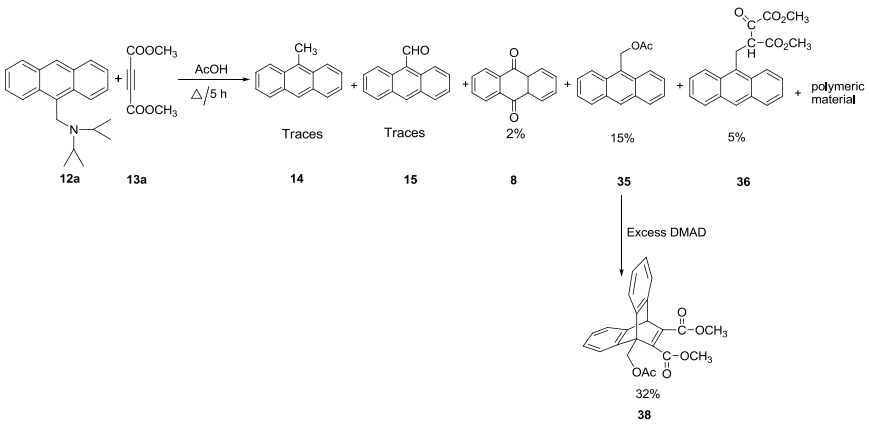


Scheme 3.21

We can see competing electron transfer reactions in acetic acid when reaction is carried out at low concentration of (anthracen-9-yl)methanamines **12a-f**. Here the competition is between one electron transfer and two electron transfer reactions in which two electron transfer reaction is the major pathway.

To study the effect of concentration we carried out the reaction of 0.34 M solution of **12a** in acetic acid with three equivalents of **13a** which gave Diels-Alder adduct[45] **38** formed between **35** and **13a** (Scheme **3.22**). Under these conditions, the

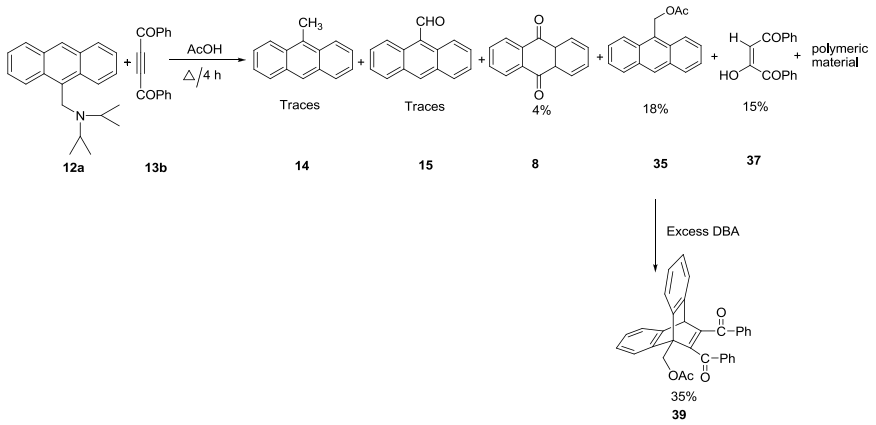
Diels-Alder adduct was formed along with the other products formed under dilute condition.



Scheme 3.22

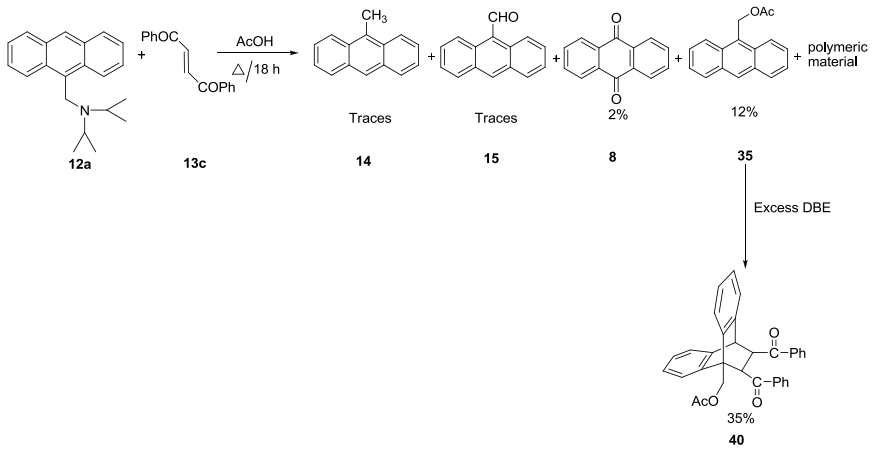
At higher concentration, **13b** also reacted in the same way as **13a** with **12a** (Scheme **3.23**).

In a blank run involving the reaction of **35** with **13a-c** in acetic acid, we observed that the corresponding Diels-Alder adducts **38**, **39** and **40** respectively were generated in appreciable amounts indicating that Diels-Alder reaction is viable in boiling acetic acid.



Scheme 3.23

Though DBE (**13c**) has less reactivity compared to **13a** and **13b**, at higher concentration **13c** reacted in the same way with **12a** to give corresponding products (Scheme **3.24**).



Scheme 3.24

Figure **3.1** shows the ORTEP diagram of Diels-Alder adduct **40**.

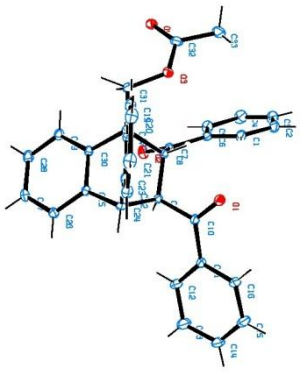


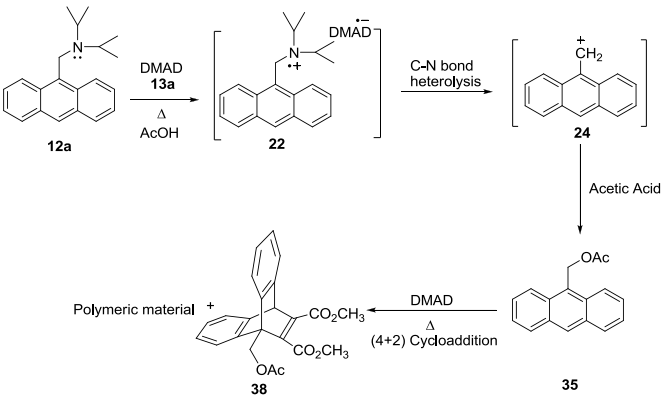
Figure 3.1

To check the role of dienophiles in the generation of products such as **14**, **15**, **8** and **35**, we refluxed (anthracen-9-yl)methanamines alone in acetic acid for 15h. Unchanged starting material was recovered in quantitative amounts at the end of the reaction indicating direct involvement of dienophile in the formation of these products.

In order to establish the generality of this reaction, we repeated the reaction using different (anthracen-9-yl)methanamines **12b-e**. All the above (anthracen-9-yl)methanamines **12b-e** reacted in the same way and resulted in the same products in comparable yields.

Though generation of **35** suggests mechanism similar to that observed in methanol, absence of **25** and generation of new products such as **36** and **37** was baffling and the mechanism of reactions in acetic acid is uncertain. Specifically, the mechanism of C-N bond cleavage is debatable. It may occur through two different pathways. One attractive possibility is the reaction taking place

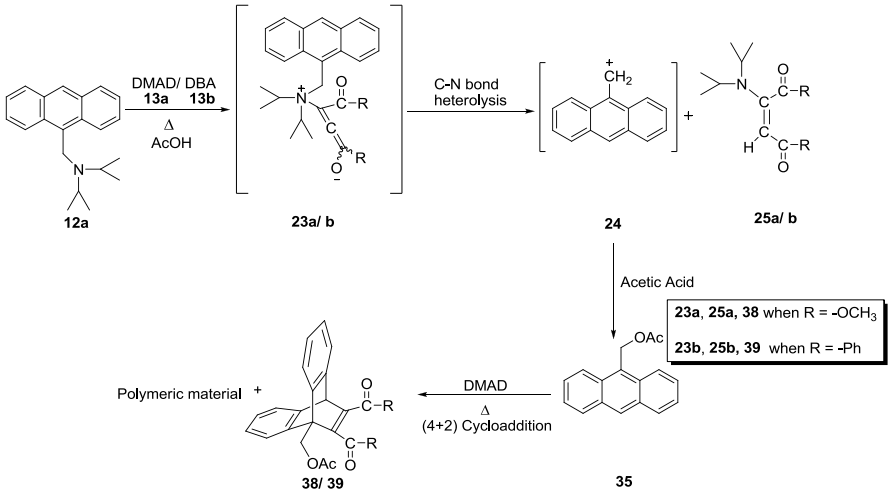
through initial one electron transfer, from the (anthracen-9-yl)methanamines to dienophiles which leads to the formation of radical anion-radical cation pair **22**, followed by C-N bond heterolysis to form 9-anthracenemethyl cation (**24**). It is captured by solvent molecule to form **35**. The overall mechanism here may be interpreted as electron transfer mediated nucleophilic substitution reaction. Diels-Alder addition takes place between **35** and dienophiles **13a** yielding corresponding cycloadduct. The general mechanism of reaction between (anthracen-9-yl)methanamines and **13a** is shown in Scheme **3.25**. The mechanism depicted in Scheme **3.25**, however, does not account for the formation of products such as **36** and **37**. Hence, other mechanistic possibilities also should be considered.



Scheme 3.25

Second possibility is the reaction proceeding through nucleophilic attack of (anthracen-9-yl)methanamines **12a-h** with dienophiles **13a-b** in a Michael type addition pathway which leads

to the weakening and eventual cleavage of C-N bond giving rise to 9-anthracenemethyl cation (**24**) and *N*,*N*-dialkylaminomaleate or 2-dialkylaminodibenzoylethylene as was the case with methanol reactions. The anthracenemethyl cation (**24**) formed is captured by acetic acid to give **35**. Subsequently, **35** undergoes [4+2] cycloaddition with excess dienophile **13a-b** present in the reaction mixture to give the corresponding Diels-Alder adducts. In scheme **3.26**, the second possibility is illustrated by taking **12a** with **13a/b** as examples.



Scheme 3.26

If the reaction proceeds through the above mechanism, Michael adduct **25a/b** should also be generated. With a view to ascertain this possibility, we carried out GC-MS and NMR analyses of the crude product mixture. The results indicated the absence of Michael adducts **25a/b** in the reaction mixture. So we concluded that **25a** or **25b** are either not formed or undergo further

transformations under the reaction conditions employed by us. To discount the latter possibility, we treated independently synthesized Michael adducts (**Chart 3.2**) by supplying same conditions of acetic acid reactions.

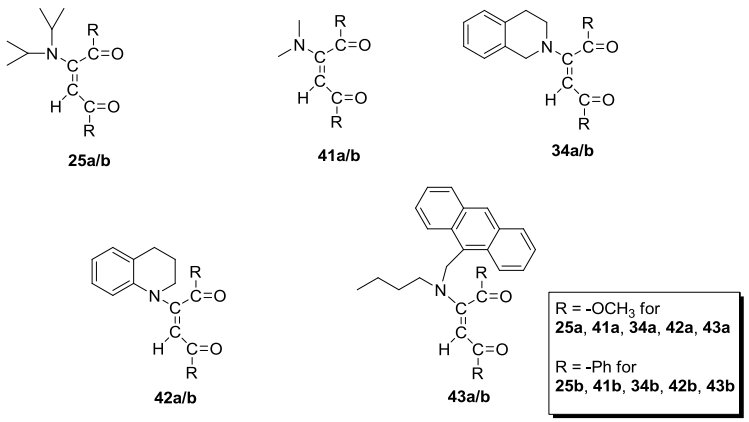


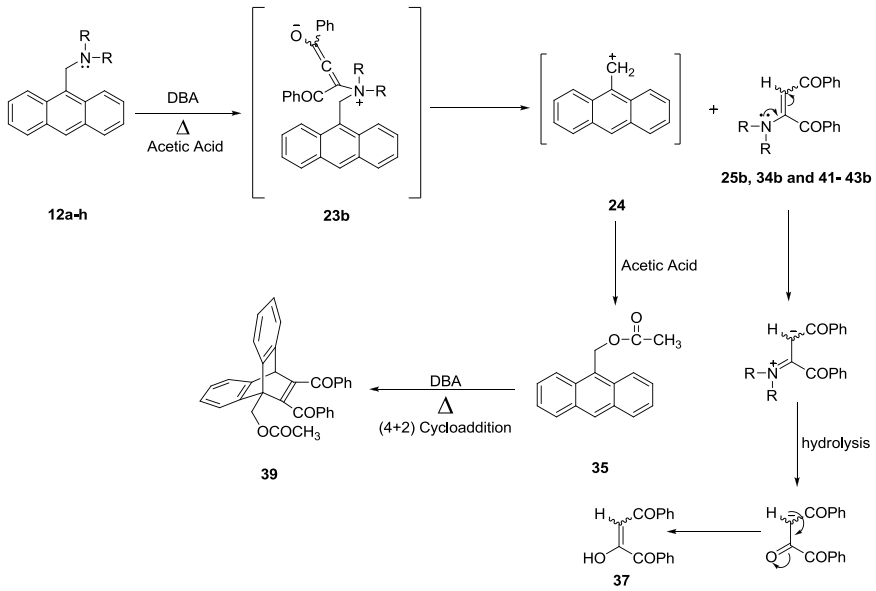
Chart 3.2

Michael adducts were synthesised by stirring secondary amine and dienophile under room temperature. After 10 minutes we could easily separate the Michael adduct in high yield. When the directly synthesized Michael adducts (**25a**, **34a** and **41-43a**) were refluxed with two equivalents of DMAD (**13a**) in acetic acid, the reaction was completed in 4h. Michael adducts underwent extensive decomposition and we could not separate any products from the reaction mixtures. Extensive decomposition of Micahel adducts to intractable mixture was observed even when the adducts were refluxed with acetic acid in the absence of DMAD. From these

results, we could neither confirm nor rules out the involvement of Michael adducts in the course of the reaction.

The story is different in the case of fourth adduct **43a**. After 4h, the reaction of **43a** with DMAD yielded **15**, **8** and **35** along with polymeric materials. But here also we could not isolate the amine component. Similar products may be formed in the decomposition of **25a**, **34a**, **41a**, and **42a**, but the products formed are volatile and hence escaped isolation/detection.

We repeated the above procedure using DBA adducts (**25b**, **34b** and **41-43b**). Refluxing Michael adducts (**25b**, **34b** and **41-42b**) with DBA in acetic acid for about 4h results in 2-hydroxydibenzoylethylene (**37**) and polymerised materials. Michael adduct **43b** also reacted in the same way yielding **39**, along with **15**, **8** and **37** (Scheme **3.27**). This result shows that 2-hydroxydibenzoylethylene (**37**) is formed from Michael adducts **25b**, **34b** and **41-43b**.

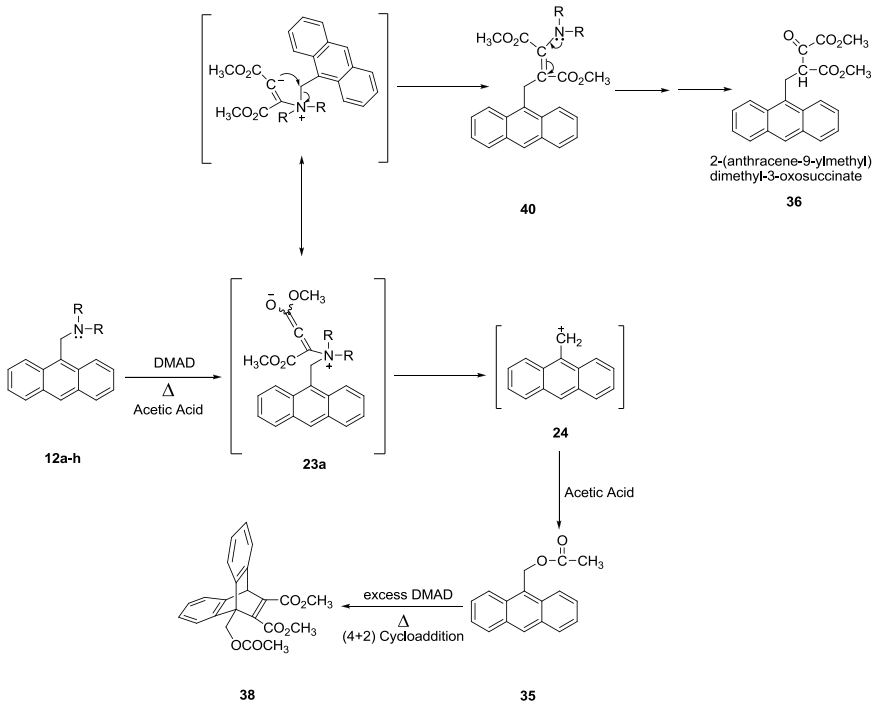


Scheme 3.27

We have repeated the reactions of **25a/b**, **34a/b** and **41-43a/b** with **13a/b** without dienophiles, both in thermal and room temperature. Rate of the reactions are very low under above conditions and yielded same products along with unreacted starting materials in different yields. Consequently, it is possible that Michael adducts are generated in the reaction between anthracenemethanamines and DBA but go undetected due to fast decomposition. Furthermore, generation of Michael adducts mandates zwitterion **23b** as a possible intermediate in the reaction of **12a** with DBA. We further argue that what is true for DBA reaction should be true for DMAD reaction as well. Hence, we can safely argue that zwitterion **23a** is a possible intermediate in the reaction between **12a** and DMAD. Thus we conclude that the reaction between anthracenmethanamines and dienophiles proceed

through initial Michael type addition pathway generating zwitterionic intermediates identical to those observed in the methanol reaction. Major difference here is that Michael adducts undergo fast decomposition and hence elude detection in refluxing acetic acid. Decomposition of Michael adducts is accelerated by dienophile present in the reaction medium.

Providing further support to the mechanism involving zwitterionic intermediate, formation of **36** can also explained on the basis of zwitterionic intermediate **23a**. C to N migration in zwitterion **23a-h** formed by the Michael addition of (anthracen-9-yl)methanamines **12a-h** with **13a** leads to the formation **40**. It undergoes hydrolysis to yield **36** (Scheme **3.28**).



Scheme 3.28

We observed different types of competing reactions in acetic acid medium. Irrespective of concentration, single electron transfer mode is a minor pathway, two electron transfer pathway predominates. At higher concentrations, Diels-Alder pathway also becomes significant.

Earlier studies from our group revealed that the reaction of (anthracen-9-yl)methanamines **12a-e** with dienophiles in propionic acid also proceeded through the same pathway as with acetic acid reactions. We have also examined the reactions of **12a-e** with dienophiles in both trifluoroacetic acid and formic acid.[40] Here formation of stable salts prevented both single and two electron

transfer reactions. Diels-Alder reactions of these salts are not feasible in low boiling solvents. So neither electron transfer nor cycloaddition pathways were operating in these cases.

3.4. Conclusion

We have illustrated interesting solvent and concentration dependent reactions of a few (anthracen-9-yl)methanamines with dienophiles and explored the mechanistic pathways of these reactions under different conditions. Depending on the nature of solvent, the mechanism of the reaction changes from radical to ionic pathways. When the concentration of the reactants increases Diels-Alder pathway predominates. We performed the reaction in solvents such as xylene, acetonitrile, DMF, methanol and acetic acid at low and high concentrations.

In summary, we conclude that electron-transfer mediated homolytic C-N bond cleavage followed by dimerization and intramolecular Diels-Alder reaction to form lepidopterene is the major reaction under nonpolar and polar aprotic solvents. Trace amounts of products arising through reaction with adventitious oxygen are formed in most cases. At higher concentration, the major pathway is [4+2] cycloaddition. On the other hand, reaction carried out in polar protic solvents proceeded through Micahel type addition followed by C-N bond cleave giving rise to anthracenemethyl cation and products derived thereof. In acetic acid medium, some of the primary products underwent extensive

decomposition.

For studying the effect of dienophiles, we have done the reaction using DBA and DBE. Rate of the reaction is directly proportional to the magnitude of electron deficiency of the dienophile. Reaction of (anthracen-9-yl)methanamines with DBA proceeds through the similar mechanism and yields similar products as with DMAD reaction under most conditions.

DBE has less reactivity than DMAD and DBA. So the reaction of (anthracen-9-yl)methanamines with DBE is very slow in comparison with DBA and DMAD reactions. However, interesting products were generated in these reactions as well.

We have demonstrated the generality of the observed transformations using a variety of anthracenemethanamines. Our results clearly indicate that the course of the reactions is not significantly altered with change in substituents around the significant nitrogen in anthracenemethanmines.

3.5. Experimental

3.5.1. General Techniques

All reactions were carried out using oven dried glasswares. All experiments were done with distilled and dried solvents by using standard protocols. All starting materials were purchased from either *Sigma-Aldrich* or *Spectrochem Chemicals* and were used without further purification. Progress of the reaction and chromatographic separations were monitored by dried and activated silica gel TLC plates (Aluminium sheets coated with silica gel, *E. Merck*). Visualisation of TLC plates was acquired by exposure to iodine vapours or UV lamp. Separation and purification of compounds were done by column chromatography using either silica gel (*Spectrochem Chemicals*, 60-120 mesh) or neutral alumina (*Spectrochem Chemicals)*. The products were further purified by recrystallization from suitable solvent systems. Solvent eluted from the column chromatography was concentrated using *Heidolph* rotary evaporator. Melting points are uncorrected and were determined on a *Neolab* melting point apparatus. Infra-red spectra were recorded using *Jasco 4100* and *ABB Bomem (MB Series)* FT-IR spectrometers. The ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz *Bruker Avance III* FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS. Elemental analysis was performed using *Elementar Systeme (Vario*

EL III). Molecular mass was determined by electron impact (EI) method using GC-MS (*Agilent GC-7890A, Mass-5975C*) and fast atom bombardment (FAB) using *JMS 600 JEOL* mass spectrometer. Here we are giving the spectral and analytical data only for novel compounds and the corresponding reference cited for known compounds.

3.5.2. Dibenzoylacetylene

Dibenzoylacetylene[10] (**13b**) was prepared by a known procedure (75%, mp 109-110 °C).

3.5.3. Dibenzoylethylene

Dibenzoylethylene[11] (**13c**) was synthesized by a known procedure (70%, mp 110-111 °C).

3.5.4. Reactions of (Anthracen-9-yl)methanamines with Dienophiles

3.5.4.1. Reactions in nonpolar medium - Xylene

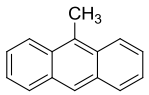
3.5.4.1.1. Reaction of 9-(*N,N*-Diisopropylaminomethyl)anthracene (12a) with DMAD (13a).

To a solution (0.034 M) of **12a** (0.700 g, 2.4 mmol) in xyle-

-ne (70 mL), DMAD (1.50 g, 10.6 mmol) was added and the mixture was refluxed for 48h. Progress of the reaction was monitored by TLC. After the reaction was complete, the reaction mixture was cooled and the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with hexane gave **14** (traces) and **15** (4%) was obtained by the elution using a mixture (4:1) of hexane and dichloromethane. Further elution with a mixture of (7:3) hexane and dichloromethane gave **16** (7%) followed by **17** (13%). Elution with mixture of (3:2) hexane and dichloromethane yielded **8** (16%).

In a repeat run, a more concentrated solution (0.34 M) of **12a** (1.50 g, 5.2 mmol) in xylene (15 mL) was refluxed with DMAD (2.22 g, 15.6 mmol) for 25h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. The major product formed is the corresponding Diels-Alder adduct **26a** (64%). This product is obtained by elution with a mixture (7:3) of hexane and ethyl acetate. Along with **26a**, trace amounts of **14**, **15** and **8** were also obtained in this reaction.

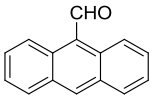
Compound 14[46]**:-**



mp:- 78-81 °C.

MS:- *m/z* 192 (M^+).

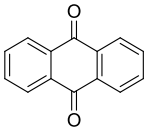
Compound 15[47]**:-**



mp:- 103-105 °C.

MS:- *m/z* 206 (M^+), 205 (M-1).

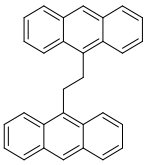
Compound 8[48]**:-**



mp:- 284-286 °C.

MS:- *m/z* 208 (M^+), 180 (M-28).

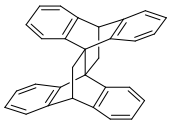
Compound 16[49]**:-**



mp:- 238-239 °C.

MS:- *m/z* 382 (M^+), 191.

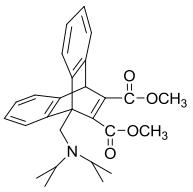
Compound 17[50]**:-**



mp:- 316-318 °C.

MS:- *m/z* 382 (M^+).

Compound 26a:-



mp:- 154-156 °C.

IR ν_{max} (KBr):- 1732, 1707 cm^{-1} (C=O stretch), 1276 cm^{-1} (C-O stretch).

^{1}H NMR ($CDCl_3$):- δ 6.98-7.85 (m, 8H), 5.55 (s, 1H), 4.00 (s, 2H), 3.76 (s, 3H), 3.75 (s, 3H), 3.24-3.31 (m, 2H), 1.17 (d, 12H, J = 6.4 Hz).

^{13}C NMR ($CDCl_3$):- δ 167.25, 164.22, 153.92, 146.15, 145.67, 142.54, 125.04, 124.54, 123.47, 123.31, 55.43, 52.33, 51.93, 51.12, 47.36, 41.78, 20.61.

MS:- *m/z* 434 (*M*+1), 418, 333, 114.

Elemental analysis calculated for

$C_{27}H_{31}NO_4$:- C: 74.80, H: 7.21, N: 3.23.

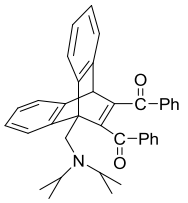
Found:- C: 74.79, H: 7.21, N: 3.23.

3.5.4.1.2. Reaction of 9-(*N,N*-Diisopropylaminomethyl)anthracene (12a) with DBA (13b).

A solution (0.034 M) of **12a** (0.700 g, 2.4 mmol) in xylene (70 mL) was refluxed with DBA (2.50 g, 10.7 mmol) for 42h. Progress of the reaction was monitored by TLC. After the reaction was complete, the reaction mixture was cooled and the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with hexane gave **14** (traces) and **15** (3%) was obtained by the elution using a mixture (4:1) of hexane and dichloromethane. Further elution with a mixture (7:3) hexane and dichloromethane gave **16** (7%) followed by **17** (14%). Elution with a mixture (3:2) of hexane and dichloromethane gave **8** (18%).

In a repeat run a more concentrated solution (0.34 M) of **12a** (1.50 g, 5.2 mmol) in xylene (15 mL), was refluxed with DBA (3.65 g, 15.6 mmol) for 23h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. The major product formed is the corresponding Diels-Alder adduct **26b** (66%). This product is obtained by elution with a mixture (3:2) hexane and ethyl acetate. Along with **26b**, trace amounts of **14**, **15** and **8** are obtained.

Compound 26b:-



mp:- 188-190 °C.

IR ν_{max} (KBr):- 1652, 1596 cm^{-1}(C=O stretch), 1268 cm^{-1}(C=O bend).

^{1}H NMR ($CDCl_3$):- δ 7.06-8.03 (m, 18H), 5.36 (s, 1H), 4.08 (s, 2H), 3.07-3.13 (m, 2H), 0.92 (d, 12H, *J* = 6.4 Hz).

^{13}C NMR ($CDCl_3$):- δ 194.93, 193.78, 151.45, 146.72, 145.54, 137.54, 136.92, 132.90, 132.85, 129.10, 129.04, 128.16, 128.12, 125.11, 124.76, 123.81, 123.44, 56.37, 53.74, 47.34, 41.93, 20.25.

MS:- *m/z* 525 (M^+), 105.

Elemental analysis calculated for

$C_{37}H_{35}NO_2$:- C: 84.53, H: 6.72, N: 2.67.

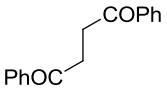
Found:- C: 84.52, H: 6.72, N: 2.68.

3.5.4.1.3. Reaction of 9-(*N,N*-Diisopropylaminomethyl)anthracene (12a) with DBE (13c).

To a solution (0.034 M) of **12a** (0.700 g, 2.4 mmol) in xylene (70 mL), DBE (2.50 g, 10.6 mmol) was added and the mixture was refluxed for 60h. The progress of the reaction was monitored by TLC and the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with hexane gave **14** (traces) and **15** (traces) was obtained by the elution using a mixture (4:1) of hexane and dichloromethane followed by **18** (16%). Further elution with a mixture (3:2) of hexane and dichloromethane gave **8** (3%) and continued elution with a mixture (1:1) of hexane and dichloro-

-methane yielded **19** (10%).

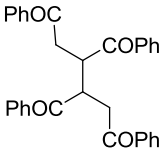
Compound 18[51]**:-**



mp:- 145-146 °C.

MS:- *m/z* 238 (M^+), 105.

Compound 19[52]**:-**



mp:- 166-167 °C.

MS:- *m/z* 474 (M^+), 105.

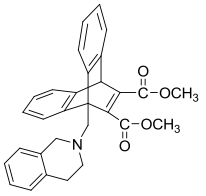
3.5.4.1.4. Reaction of *N*-((Anthracen-9-yl)methyl)-1,2,3,4-tetrahydroisoquinoline (12f) with DMAD (3a).

To a solution (0.031 M) of **12f** (0.700 g, 2.2 mmol) in xylene (70 mL), DMAD (1.20 g, 8.5 mmol) was added and the mixture was refluxed for 53h. The progress of the reaction was monitored by TLC. After the reaction was complete, the reaction mixture was cooled and the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with hexane gave **14** (traces) and **15** (2%) was obtained by the elution using a mixture of (4:1) hexane and dichloromethane. Further elution with a mixture of (7:3) hexane and dichloromethane gave **16** (3%) followed by **17** (8%). With the elution using a mixture of (3:2) hexane and dichloromethane yielded **8** (9%).

In a repeat run a more concentrated solution (0.16 M) of **12f**

(0.700 g, 2.2 mmol) in xylene (14 mL), was refluxed with DMAD (1.0 g, 7.0 mmol) for 12h. Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. The major product formed is the corresponding Diels-Alder adduct **29a** (40%). This product is obtained by elution with a mixture (7:3) hexane and ethyl acetate. Along with **29a**, trace amounts of **14**, **15** and **8** are obtained. Our attempts to purify this compound were not successful. Mass and crude ^{1}H NMR spectral data are in agreement with the proposed structure.

Compound 29a:-



MS:- *m/z* 466 (*M*+1).

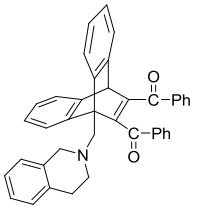
3.5.4.1.5. Reaction of *N*-((Anthracen-9-yl)methyl)-1,2,3,4-tetrahydroisoquinoline (12f) with DBA (13b).

To a solution (0.031 M) of **12f** (0.700 g, 2.2 mmol) in xylene (70 mL), DBA (0.60 g, 4.2 mmol) was added and the mixture was refluxed for 50h. Progress of the reaction was monitored by TLC.

In a repeat run, DBA (1.6 g, 6.8 mmol) was added to a solution (0.16 M) of **12f** (0.700 g, 2.2 mmol) in xylene (14 mL) and the mixture was refluxed for 18h. Solvent was removed under

reduced pressure and the residue was purified by column chromatography on silica gel. The major product formed is the corresponding Diels-Alder adduct **29b** (50%). This product is obtained by elution with a mixture (7:3) hexane and ethyl acetate. Along with **29b**, trace amounts of **14**, **15** and **8** are obtained. Our attempts to purify this compound were not successful. Mass and crude ^{1}H NMR spectral data are in agreement with the proposed structure.

Compound 29b:-



MS:- *m/z* 558 (*M*+1), 105.

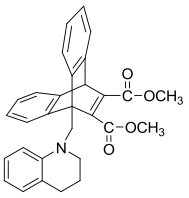
3.5.4.1.6. Reaction of *N*-((Anthracen-9-yl)methyl)-1,2,3,4-tetrahydroquinoline (12g) with DMAD (13a).

To a solution (0.015 M) of **12g** (0.350 g, 1.1 mmol) in xylene (70 mL), DMAD (0.60 g, 4.2 mmol) was added and the mixture was refluxed for 50h. Progress of the reaction was monitored by TLC. From the reaction mixture, **12g** was recovered in significant amounts along with some polymerized products.

Refluxing a solution (0.16 M) of **12g** (0.700 g, 2.2 mmol) in xylene (14 mL) with DMAD (1.0 g, 7.0 mmol) was done for 36h. The progress of the reaction was monitored by TLC. After the

reaction was complete, the reaction mixture was cooled and the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with hexane gave **14** (traces) and **15** (traces) was obtained by the elution of a mixture of (9:1) hexane and ethyl acetate followed by **8** (2%). Major product Diels-Alder adduct **30a** (58%) was obtained by the elution using a mixture (7:3) of hexane and ethyl acetate.

Compound 30a:-



mp:- 161-163 °C.

IR ν_{max} (KBr):- 1723, 1703 cm^{-1}(C=O stretch), 1276 cm^{-1}(C-O stretch).

^{1}H NMR ($CDCl_3$):- δ 6.75-7.55 (m, 12H), 5.63 (s, 1H), 4.71 (s, 2H), 3.77 (s, 3H), 3.47 (s, 3H), 3.15 (t, 2H, *J* = 5.4 Hz), 2.82 (t, 2H, *J* = 6.4 Hz), 1.86 (quin, 2H, *J* = 5.6 Hz).

^{13}C NMR ($CDCl_3$):- δ 166.55, 164.22, 146.43, 145.28, 145.18, 143.22, 129.60, 127.02, 125.43, 124.92, 124.74, 123.77, 122.32, 117.85, 113.07, 55.12, 52.44, 52.23, 51.05, 49.01, 46.66, 27.96, 21.15.

MS:- *m/z* 465 (M^+).

Elemental analysis calculated for

$C_{30}H_{27}NO_4$:- C: 77.40, H: 5.85, N: 3.00.

Found:- C: 77.39, H: 5.85, N: 3.01.

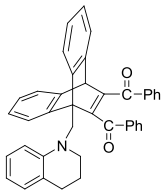
3.5.4.1.7. Reaction of *N*-((Anthracen-9-yl)methyl)-1,2,3,4-tetrahydroquinoline (12g) with DBA (13b).

To a solution (0.015 M) of **12g** (0.350 g, 1.1 mmol) in xyle-

-ne (70 mL), DBA (1.00 g, 4.3 mmol) was added and the mixture was refluxed for 50h. Progress of the reaction was monitored by TLC. From the reaction mixture, **12g** was recovered in near-quantitative amounts along with some polymerized products.

To a solution (0.16 M) of **12g** (0.700 g, 2.2 mmol) in xylene (14 mL), DBA (1.6 g, 6.8 mmol) was added and the mixture was refluxed for 38h. The progress of the reaction was monitored by TLC. When the reaction was complete, the reaction mixture was cooled and the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with hexane and a mixture of (9:1) hexane and ethyl acetate gave **14** (traces) and **15** (traces) respectively followed by **8** (3%). Further elution with a mixture (7:3) of hexane and ethyl acetate gave Diels-Alder adduct (**30b**) (60%) as the major product.

Compound 30b:-



mp:- 194-195 °C.

IR ν_{max} (KBr):- 1655(C=O stretch), 1598 cm^{-1}.

^{1}H NMR ($CDCl_3$):- δ 6.50 (m, 22H), 5.45 (s, 1H), 4.54 (s, 1H), 3.04 (t, 2H, *J* = 5.4 Hz), 2.61 (t, 2H, *J* = 6.4 Hz), 1.46-1.51 (m, 2H).

^{13}C NMR ($CDCl_3$):- δ 194.70, 192.50, 152.39, 145.91, 145.56, 145.18, 137.36, 136.72, 133.15, 132.28, 129.24, 128.28, 128.01, 126.66, 125.53, 125.10, 124.76, 123.80, 122.43, 117.89, 112.52, 56.38, 53.55, 48.94, 46.19, 27.79, 20.61.

MS:- *m/z* 557 (M^+), 105.

Elemental analysis calculated for

$C_{40}H_{31}NO_2$:- C: 86.15, H: 5.61, N: 2.51.

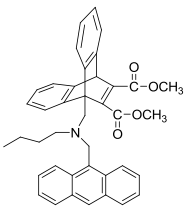
Found:- C: 86.14, H: 5.61, N: 2.51.

3.5.4.1.8. Reaction of 9-(*N,N*-Bisanthracenemethyl)butylamine (12h) with DMAD (13a).

To a solution (0.011 M) of **12h** (0.700 g, 1.5 mmol) in xylene (140 mL), DMAD (0.64 g, 4.5 mmol) was added and the mixture was refluxed for 50h. Progress of the reaction was monitored by TLC. From the reaction mixture, **12h** was recovered in significant amounts along with some polymerized materials.

DMAD (0.64 g, 4.5 mmol) was added to a solution (0.11 M) of **12h** (0.700 g, 1.5 mmol) in xylene (14 mL) and the mixture was refluxed for 15h. After the reaction was complete, the reaction mixture was cooled and the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with hexane and a mixture 4:1) of hexane and dichloromethane gave **14** (traces) and **15** (traces) respectively followed by **8** (2%). Further elution with a mixture of (1:1) hexane and dichloromethane gave **31a** (23%). Elution using a mixture of (1:4) hexane and dichloromethane gave **32a** (33%).

Compound 31a:-



mp:- 169-171 °C.

IR ν_{max} (KBr):- 1712(C=O stretch), 1620 cm^{-1}, 1274 cm^{-1}(C-O stretch).

^{1}H NMR ($CDCl_3$):- δ 6.82-8.68 (m, 17H), 5.42 (s, 1H), 4.85 (s, 2H), 3.88 (s, 2H), 3.64 (s, 3H), 3.13 (s, 3H), 2.76 (t, 2H, *J* = 7.8 Hz), 1.88-1.92 (m, 2H), 1.19-1.26 (m, 2H), 0.83 (t, 3H, *J* = 7.4 Hz).

^{13}C NMR ($CDCl_3$):- δ 166.72, 164.29, 153.81, 145.32, 144.85, 143.34, 131.57, 131.56, 130.01, 129.19, 127.80, 125.71, 125.20, 125.02, 124.90, 124.55, 124.35, 123.23, 55.92, 54.75, 52.22, 51.46, 51.12, 51.08, 50.81, 29.59, 20.92, 14.04.

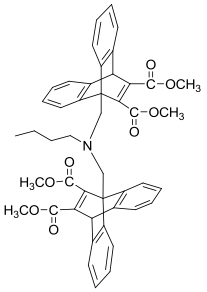
MS:- *m/z* 595 (M^+), 191.

Elemental analysis calculated for

$C_{40}H_{37}NO_4$:- C: 80.65, H: 6.25, N: 2.34.

Found:- C: 80.64, H: 6.26, N: 2.35.

Compound 32a:-



mp:- 104-106 °C.

IR ν_{max} (KBr):- 1718 (C=O stretch), 1619 cm^{-1}, 1262 cm^{-1}(C-O stretch).

^{1}H NMR ($CDCl_3$):- δ 6.93-7.85 (m, 16H), 5.47 (s, 2H), 4.23 (s, 4H), 3.68 (s, 6H), 3.53 (s, 6H), 2.62 (t, 2H, *J* = 7.8 Hz), 1.56-1.60 (m, 2H), 0.98-1.04 (m, 2H), 0.64 (t, 3H, *J* = 7.2 Hz).

^{13}C NMR ($CDCl_3$):- δ 167.08, 164.57, 152.87, 145.20, 145.00, 144.23, 125.30, 124.89, 123.91, 123.47, 56.14, 55.85, 52.40, 52.13, 52.00, 51.35, 30.76, 20.63, 13.87.

MS:- *m/z* 737 (M^+), 272, 84.

Elemental analysis calculated for

$C_{46}H_{43}NO_8$:- C: 74.86, H: 5.88, N: 1.90.

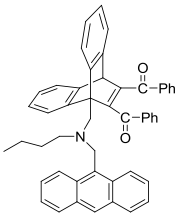
Found:- C: 74.85, H: 5.87, N: 1.91.

3.5.4.1.9. Reaction of 9-(*N,N*-Bisanthracenemethyl)butylamine (12h) with DBA (13b).

To a solution (0.011 M) of **12h** (0.700 g, 2.2 mmol) in xylene (140 mL), DBA (2.00 g, 8.5 mmol) was added and the mixture was refluxed for 50h. Progress of the reaction was monitored by TLC. Workup of the reaction mixture gave unchanged **12h** in near-quantitative amounts along with some polymerized materials.

DBA (1.05 g, 4.5 mmol) was added to a solution (0.11 M) of **12h** (0.700 g, 1.5 mmol) in xylene (14 mL) and the mixture was refluxed for 18h. The progress of the reaction was monitored by TLC. After the reaction was complete, the reaction mixture was cooled and the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with hexane gave **14** (traces) and **15** (traces) was obtained by the elution using a mixture of (4:1) hexane and dichloromethane. Elution with a mixture (3:2) of hexane and dichloromethane gave **8** (2%). Further elution with a mixture (1:1) of hexane and dichloromethane gave **31b** (26%). Elution using a mixture (2:8) of hexane and dichloromethane gave **32b** (37%).

Compound 31b:-



mp:- 174-176 °C.

IR ν_{max} (KBr):- 1650 (C=O stretch), 1590 cm^{-1}.

^{1}H NMR ($CDCl_3$):- δ 6.76-7.90 (m, 27H), 5.18 (s, 1H), 4.56 (s, 2H), 3.97 (s, 2H), 2.52 (t, 2H, *J* = 7.8 Hz), 1.43-1.45 (m, 2H), 0.82-0.88 (m, 2H), 0.57 (t, 3H, *J* = 7.4 Hz).

^{13}C NMR ($CDCl_3$):- δ 194.13, 192.60, 152.32, 151.31, 144.80, 144.08, 136.29, 135.88, 131.86, 131.60, 130.62, 130.40, 128.81, 128.12, 127.90, 127.86, 127.10, 126.85, 126.78, 124.56, 124.09, 123.96, 123.79, 123.69, 122.81, 122.16, 54.75, 52.74, 49.51, 49.34, 28.42, 19.66, 12.88.

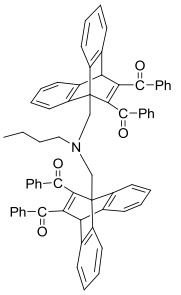
MS:- *m/z* 687 (M^+), 191, 105.

Elemental analysis calculated for

$C_{50}H_{41}NO_2$:- C: 87.31, H: 6.01, N: 2.04.

Found:- C: 87.30, H: 6.01, N: 2.04.

Compound 32b:-



mp:- 139-141 °C.

IR ν_{max} (KBr):- 1653, 1590 cm^{-1} (C=O stretch).

^{1}H NMR ($CDCl_3$):- δ 6.93-7.47 (m, 36H), 5.33 (s, 2H), 4.32 (s, 4H), 2.31 (t, 2H, *J* = 8.0 Hz), 0.85-0.88 (m, 4H), 0.31 (t, 3H, *J* = 7.2 Hz).

^{13}C NMR ($CDCl_3$):- δ 195.26, 193.87, 152.64, 146.01, 144.90, 137.64, 136.92, 133.02, 132.94, 129.37, 129.00, 128.21, 128.18, 125.06, 124.91, 123.33, 123.25, 57.86, 53.75, 52.97, 19.94, 13.57.

MS:- *m/z* 921 (M^+), 105.

Elemental analysis calculated for

$C_{66}H_{51}NO_4$:- C: 85.95, H: 5.59, N: 1.55.

Found:- C: 85.96, H: 5.59, N: 1.55.

3.5.4.2. Reactions in polar aprotic media – DMF and Acetonitrile

Procedures for the reactions in polar aprotic media are similar to those applied for reactions in nonpolar medium-xylene. But the reaction time and yields are different. We are presenting only the concentration, reaction time and yield of each product. Most of these reactions were accompanied by extensive polymerization of dienophile and decomposition of amine to give polar, intractable mixture along with isolable products in low yields. Only products isolated in pure form are reported hereunder.

3.5.4.2.1. Reaction of 9-(*N,N*-Diisopropylaminomethyl)anthracene (12a) with DMAD (13a) in Acetonitrile.

In refluxing acetonitrile, a 0.034 M solution of **12a** on treatment with 4 equivalents of **13a** for 80h gave a mixture of **14** (traces), **15** (2%) and **8** (12%).

3.5.4.2.2. Reaction of 9-(*N,N*-Diisopropylaminomethyl)anthracene (12a) with DMAD (13a).

In refluxing DMF, a 0.034 M solution of **12a** on treatment with 4 equivalents of **13a** for 35h gave a mixture of **14** (traces), **15** (4%), **8** (18%), **16** (7%) and **17** (14%).

In a repeat run, a 0.34 M solution of **12a** with 3 equivalents of **13a** for 20h gave a mixture of **14** (traces), **15** (traces), **8** (traces) and **29a** (58%).

3.5.4.2.3. Reaction of 9-(*N,N*-Diisopropylaminomethyl)anthracene (12a) with DBA (13b).

Treating 0.034 M solution of **12a** in refluxing DMF with 4 equivalents of **13b** for 30h gave a mixture of **14** (traces), **15** (6%), **8** (16%), **16** (7%) and **17** (13%).

In a repeat run, a 0.34 M solution of **12a** with 3 equivalents of **13b** for 20h gave a mixture of **14** (traces), **15** (traces), **8** (traces) and **29b** (64%).

3.5.4.2.4. Reaction of 9-(*N,N*-Diisopropylaminomethyl)anthracene (12a) with DBE (13c).

In refluxing DMF, a 0.034 M solution of **12a** on treatment with 4 equivalents of **13c** for 55h gave a mixture of **14** (traces), **15** (traces), **8** (3%), **18** (14%) and **19** (9%) with unreacted starting materials (40%).

3.5.4.2.5. Reaction of *N*-((Anthracen-9-yl)methyl)-1,2,3,4-tetrahydroisoquinoline (12f) with DMAD (13a).

In refluxing DMF, a 0.031 M solution of **12f** on treatment with 4 equivalents of 1**3a** for 54h gave a mixture of **14** (traces), **15** (3%), **8** (9%), **16** (3%) and **17** (7%).

In a repeat run, a 0.16 M solution of **12f** with 3 equivalents of **13a** for 10h gave a mixture of **14** (traces), **15** (2%), **8** (8%) and **29a** (40%).

3.5.4.2.6. Reaction of *N*-((Anthracen-9-yl)methyl)-1,2,3,4-tetrahydroisoquinoline (12f) with DBA (13b).

In refluxing DMF, a 0.031 M solution of **12f** on treatment with 4 equivalents of **13b** for 50h gave a mixture of **14** (traces), **15** (2%), **8** (10%), **16** (3%) and **17** (6%).

In a repeat run, a 0.16 M solution of **12f** with 3 equivalents of 1**3b** for 20h gave a mixture of **14** (traces), **15** (3%), **8** (12%) and **29b** (48%).

3.5.4.2.7. Reaction of *N*-((Anthracen-9-yl)methyl)-1,2,3,4-tetrahydroquinoline (12g) with DMAD (13a).

In refluxing DMF, a 0.015 M solution of **12g** on treatment with 4 equivalents of **13a** for 50h gave some polymerized materials along with unchanged **12g**.

In a repeat run, a 0.16 M solution of **12g** on treatment with 3 equivalents of **13a** for 40h gave a mixture of **14** (traces), **15** (traces), **8** (3%) and **30a** (55%).

3.5.4.2.8. Reaction of *N*-((Anthracen-9-yl)methyl)-1,2,3,4-tetrahydroquinoline (12g) with DBA (13b).

In refluxing DMF, a 0.015 M solution of **12g** on treatment with 4 equivalents of **13b** for 50h gave some polymerized materials along with unchanged **12g**.

In a repeat run, a 0.16 M solution of **12g** on treatment with 3 equivalents of **13b** for 31h gave a mixture of **14** (traces), **15** (traces), **8** (3%) and **30b** (58%).

3.5.4.2.9. Reaction of 9-(*N*,*N*-Bisanthracenemethyl)butylamine (12h) with DMAD (13a).

In refluxing DMF, a 0.011 M solution of **12h** on treatment with 4 equivalents of **13a** for 50h yielded some polymerized materials along with unchanged **12h**.

In a repeat run, a 0.11 M solution of **12h** on treatment with 3 equivalents of **3a** for 20h gave a mixture of **14** (traces), **15** (traces), **8** (3%), **31a** (21%) and **32a** (30%).

3.5.4.2.10. Reaction of 9-(*N,N*-Bisanthracenemethyl)butylamine (12h) with DBA (13b).

In refluxing DMF, a 0.011 M solution of **12h** on treatment with 4 equivalents of **13b** for 50h gave some polymerized materials along with unchanged **12h**.

In a repeat run, a 0.11 M solution of **12h** on treatment with 3 equivalents of **13b** for 23h gave a mixture of **14** (traces), **15** (traces), **8** (2%), **31b** (23%) and **32b** (35%).

3.5.4.3. Reactions in polar protic medium – Alcohol, Methanol

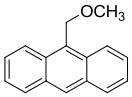
Due to low solubility of **12a-e** in methanol, all reactions were carried out at low concentration. Samples were prepared by dissolving appropriate amine in minimum amount of boiling dichloromethane followed by addition of hot methanol until the solution turned turbid. Turbidly was removed by addition of a few drops of dichloromethane and the mixture was refluxed with appropriate dienophile until **12a-e** were totally consumed. Typically a 1:10 mixture of dichloromethane and methanol was used in these experiments.

3.5.4.3.1. Reaction of 9-(*N,N*-Diisopropylaminomethyl)anthracene (12a) with DMAD (13a).

DMAD (0.51 g, 3.6 mmol) was added to a solution of **12a** (0.700 g, 2.4 mmol) in methanol-dichloromethane and the mixture

was refluxed for 10h. Progress of the reaction was monitored by TLC. When the reaction was complete, reaction mixture was cooled and the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with hexane and a mixture (4:1) of hexane and dichloromethane gave **14** (traces) and **15** (traces) respectively. Elution using a mixture (3:2) of hexane and dichloromethane yielded **8** (2%). Further elution with a mixture (1:1) of hexane and dichloromethane gave **33** (57%). Elution with a mixture (1:4) of hexane and dichloromethane gave **25a** (36%).

Compound 33[53]:-



mp:- 88-90 °C.

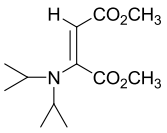
MS:- *m/z* 222 (M^+), 191.

Compound 25a:-

mp:- 93-95 °C.

IR ν_{max} (KBr):- 1739, 1686 (C=O stretch), 1131 (C-O stretch).

^{1}H NMR ($CDCl_3$):- 4.77 (s, 1H), 3.92 (s, 3H), 3.65 (s, 3H), 3.61-3.68 (m, 2H), 1.29 (d, 12H, *J* = 6.8 Hz).



^{13}C NMR ($CDCl_3$):- δ 168.14, 166.66, 152.39, 84.46, 52.81, 50.60, 19.99.

MS:- *m/z* 243 (M^+).

Elemental analysis calculated for

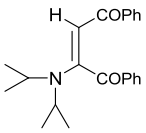
$C_{12}H_{21}NO_4$:- C: 59.23, H: 8.70, N: 5.76.

Found:- C: 59.22, H: 8.72, N: 5.76.

3.5.4.3.2. Reaction of 9-(*N,N*-Diisopropylaminomethyl)anthracene (12a) with DBA (13b).

Treating 1.5 equivalents of **13b** with **12a** for 14h in refluxing methanol-dichloromethane gave a mixture of **14** (traces), **15** (traces), **8** (traces), **33** (60%) and **25b** (31%).

Compound 25b:-



mp:-115-117 °C.

IR ν_{max} (KBr):- 1686, 1617 (C=O stretch).

^{1}H NMR ($CDCl_3$):- 7.33-8.04 (m, 10H), 6.16 (s, 1H), 3.80 (br s, 2H), 0.99-1.63 (br, 12H).

^{13}C NMR ($CDCl_3$):- δ 194.20, 185.71, 159.19, 139.78, 136.21, 133.06, 131.00, 128.81, 128.10, 127.82, 127.51, 93.30, 20.11.

MS:- *m/z* 335 (M^+), 105.

Elemental analysis calculated for

$C_{22}H_{25}NO_2$:- C: 78.76, H: 7.52, N: 4.18.

Found:- C: 78.75, H: 7.52, N: 4.19.

3.5.4.3.3. Reaction of 9-(*N,N*-Diisopropylaminomethyl)anthracene (12a) with DBE (13c).

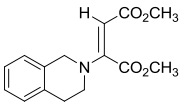
To a solution of **12a** (0.700 g, 2.4 mmol) in methanol, DBE (0.85 g, 3.6 mmol) was added and the mixture was refluxed for 60h. The progress of the reaction was monitored by TLC and the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with

a mixture of (4:1) hexane and dichloromethane gave trace amount of **15**.

3.5.4.3.4. Reaction of *N*-((Anthracen-9-yl)methyl)-1,2,3,4-tetrahydroisoquinoline (12f) with DMAD (13a).

Treating 1.5 equivalents of **13a** with **12f** for 10h in refluxing methanol gave a mixture of **14** (traces), **15** (traces), **8** (3%), **33** (46%) and **34a** (36%).

Compound 34a:-



IR ν_{max} (KBr):- 1739, 1692 cm^{-1} (C=O stretch), 1150 cm^{-1}(C-O stretch).

^{1}H NMR ($CDCl_3$):- 7.14-7.21 (m, 4H), 4.76 (s, 1H), 4.31 (s, 2H), 3.86 (s, 3H), 3.56 (s, 3H), 3.38 (t, 2H, *J* = 6 Hz), 2.86 (t, 2H, *J* = 5.8 Hz).

^{13}C NMR ($CDCl_3$):- δ 168.10, 166.08, 154.11, 134.17, 131.80, 128.35, 127.09, 126.72, 126.27, 85.20, 53.05, 50.86, 48.64, 45.49, 28.96.

MS:- *m/z* 275 (M^+).

Elemental analysis calculated for

$C_{15}H_{17}NO_4$:- C: 65.43, H: 6.23, N: 5.09.

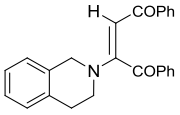
Found:- C: 65.44, H: 6.23, N: 5.09.

3.5.4.3.5. Reaction of *N*-((Anthracen-9-yl)methyl)-1,2,3,4-tetrahydroisoquinoline (12f) with DBA (13b).

Treating 1.5 equivalents of 1**3b** with **12f** for 16h in refluxi-

-ng methanol gave a mixture of **14** (traces), **15** (traces), **8** (4%), **33** (48%) and **34b** (31%).

Compound 34b:-



mp:- 64-66 °C.

IR ν_{max} (KBr):- 1675, 1614 cm^{-1} (C=O stretch).

^{1}H NMR ($CDCl_3$):- 7.08-7.98 (m, 14H), 6.08 (s, 1H), 4.46-4.58 (br, 2H), 3.45-3.52 (br, 2H), 2.73-2.83 (br, 2H).

^{13}C NMR ($CDCl_3$):- δ 199.00, 185.93, 159.80, 134.85, 132.41, 130.43, 127.95, 127.15, 127.12, 126.76, 126.27, 125.86, 125.25, 91.94, 48.14, 44.70, 28.68.

MS:- *m/z* 367 (M^+), 132, 105.

Elemental analysis calculated for

$C_{25}H_{21}NO_2$:- C: 81.72, H: 5.76, N: 3.81.

Found:- C: 81.72, H: 5.77, N: 3.81.

3.5.4.4. Reactions in polar protic medium – Acid, Acetic Acid

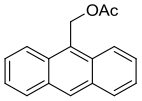
3.5.4.4.1. Reaction of 9-(*N,N*-Diisopropylaminomethyl)anthracene (12a) with DMAD (13a).

A 0.034 M solution of **12a** (0.700 g, 2.4 mmol) in acetic acid (70 mL) was refluxed with DMAD (0.68 g, 4.8 mmol) for 8h. The progress of the reaction was monitored by TLC. When the reaction was complete, the reaction mixture was washed with a saturated solution of sodium bicarbonate and extracted with DCM. Organic extracts were combined, dried over anhydrous Na_2SO_4 and

concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with hexane and a mixture of (4:1) hexane and dichloromethane gave **14** (traces) and **15** (traces) respectively. Elution with a mixture (3:2) of hexane and dichloromethane yielded **8** (2%). Further elution with a mixture (1:1) of hexane and dichloromethane gave **35** (42%). Elution using a mixture of (2:3) hexane and dichloromethane gave **36** (11%).

In a repeat run, a 0.34 M of **12a** (1.50 g, 5.2 mmol) in acetic acid (15 mL) was refluxed for 5h with DMAD (2.22 g, 15.6 mmol) under nitrogen atmosphere. Dibenzobarrelene **38** (32%) was the major product under these conditions. This product wass obtained by using a mixture (7:3) hexane and ethyl acetate as eluent. Along with **38**, minor products such as **14** (traces), **15** (traces), **8** (2%), **35** (15%) and **36** (5%) were also obtained.

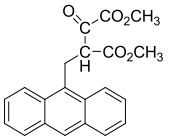
Compound 35[54]:-



mp:- 108-110 °C.

MS:- *m/z* 250 (M^+), 191.

Compound 36:-



IR ν_{max} (KBr):- 1737, 1676, 1650 cm^{-1} (C=O stretch), 1255, 1209 cm^{-1}(C-O stretch).

^{1}H NMR ($CDCl_3$):- 7.45-8.39 (m, 9H), 4.56 (t, 1H, *J* = 7.3 Hz), 4.37 (dd, 1H, *J* = 15 and 7 Hz), 4.24 (dd, 1H, *J* = 15 and 8 Hz), 3.73 (s, 3H), 3.48 (s, 3H).

^{13}C NMR ($CDCl_3$):- δ 188.09, 169.31, 160.35, 131.50,

129.97, 129.41, 129.02, 127.38, 126.26, 124.98, 123.82, 55.23, 53.26, 52.66, 25.36.

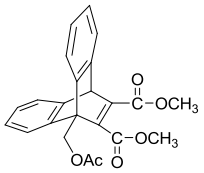
MS:- *m/z* 350 (M^+), 233, 203,191.

Elemental analysis calculated for

$C_{21}H_{18}O_5$:- C: 71.97, H: 5.19.

Found:- C: 71.98, H: 5.19.

Compound 38:-



mp:- 161-163 °C.

IR ν_{max} (KBr):- 1715 cm^{-1}(C=O stretch), 1231 cm^{-1}(C-O stretch).

^{1}H NMR ($CDCl_3$):- 7.02-7.40 (m, 8H), 5.61 (s, 1H), 5.43 (s, 2H), 3.75 (s, 3H), 3.74 (s, 3H), 2.12 (s, 3H).

^{13}C NMR ($CDCl_3$):- δ 170.62, 166.89, 163.93, 150.97, 145.46, 143.84, 142.88, 125.62, 125.32, 123.92, 121.75, 60.94, 54.87, 52.45, 52.22, 50.76, 20.63.

MS:- *m/z* 392 (M^+).

Elemental analysis calculated for

$C_{23}H_{20}O_6$:- C: 70.40, H: 5.13.

Found:- C: 81.57, H: 5.64.

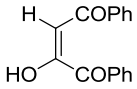
3.5.4.4.2. Reaction of 9-(*N,N*-Diisopropylaminomethyl)anthracene (12a) with DBA (13b).

To a 0.034 M solution of **12a** (0.700 g, 2.4 mmol) in acetic acid (70 mL), DBA (1.12 g, 4.8 mmol) was added and the mixture was refluxed for 6h. Progress of the reaction was monitored by TLC. When the reaction was complete, most of acetic acid was removed under reduced pressure and the residue was washed with a saturated solution of sodium bicarbonate and extracted with DCM.

Organic extracts were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue obtained was purified by column chromatography on silica gel. Elution with hexane gave **14** (traces) and **15** (traces) was obtained by the elution using a mixture of (4:1) hexane and dichloromethane. Elution with a mixture of (3:2) hexane and dichloromethane yielded **8** (4%). Further elution with a mixture of (1:1) hexane and dichloromethane gave **35** (46%). Further elution with a mixture (2:3) of hexane and dichloromethane gave **37** (17%).

In a repeat run, a 0.34 M solution of **12a** (1.50 g, 5.2 mmol) in acetic acid (15 mL) with DBA (3.65 g, 15.6 mmol) was refluxed for 4h. The residue obtained after reaction workup was purified by column chromatography on silica gel. The major product formed is the corresponding Diels-Alder adduct **39**. This product was obtained by elution with a mixture (3:2) of hexane and ethyl acetate. Along with **39**, other products **14** (traces), **15** (traces), **8** (3%), **35** (18%) and **37** (15%) were also obtained.

Compound 37:-



mp:- 61-63 °C.

IR ν_{max} (KBr):- 3437 cm^{-1} (O-H stretch), 1677, 1599 cm^{-1} (C=O stretch), 1265 cm^{-1} (C-O stretch).

^{1}H NMR ($CDCl_3$):- 7.48-8.15 (m, 10H), 6.86 (s, 1H).

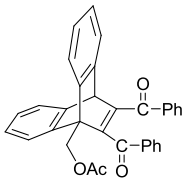
^{13}C NMR ($CDCl_3$):- δ 190.51, 187.10, 182.35, 134.29, 134.24, 133.72, 133.47, 130.49, 128.88, 128.66, 127.60, 96.24.

MS:- *m/z* 253 (M+1), 105.

Elemental analysis calculated for

$C_{16}H_{12}O_3$:- C: 76.16, H: 4.80.
Found:- C: 76.16, H: 4.79.

Compound 39:-



mp:- 207-209 °C.

IR ν_{max} (KBr):- 1744, 1656, 1593 cm^{-1} (C=O stretch), 1230 cm^{-1} (C-O stretch).

^{1}H NMR ($CDCl_3$):- 7.09-7.49 (m, 18H), 5.60 (s, 1H), 5.47 (s, 1H), 1.36 (s, 3H).

^{13}C NMR ($CDCl_3$):- δ 194.90, 193.79, 170.18, 153.67, 151.09, 145.63, 143.27, 137.59, 137.26, 132.98, 132.94, 129.08, 128.50, 125.66, 125.42, 123.92, 121.83, 60.62, 56.11, 52.91, 19.64.

MS:- *m/z* 484 (M^+), 105.

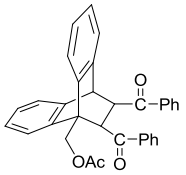
Elemental analysis calculated for
$C_{33}H_{24}O_4$:- C: 81.80, H: 5.00.
Found:- C: 81.79, H: 5.00.

3.5.4.4.3. Reaction of 9-(*N,N*-Diisopropylaminomethyl)anthracene (12a) with DBE (13c).

In refluxing acetic acid, a 0.048 M solution of **12a** on treatment with 2 equivalents of **13c** for 24h gave a mixture of **14** (traces), **15** (traces), **8** (2%) and **35** (38%).

In a repeat run, a 0.34 M solution of **12a** with 3 equivalents of **13c** for 18h gave a mixture of **14** (traces), **15** (traces), **8** (2%), **35** (12%) and **40** (35%).

Compound 40:-



mp:- 209-211 °C.

IR ν_{max} (KBr):- 1736, 1670, 1594 cm^{-1} (C=O stretch), 1245 (C-O stretch).

^{1}H NMR ($CDCl_3$):- 7.00-7.38 (m, 18H), 5.17 (d, 1H, *J* = 11.6 Hz), 4.97 (d, 1H, *J* = 11.6 Hz), 4.84 (d, 1H, *J* = 6 Hz), 4.06 (dd, 1H, *J* = 6 and 2 Hz), 1.81 (s, 3H).

^{13}C NMR ($CDCl_3$):- δ 201.55, 197.88, 170.64, 142.78, 142.40, 139.98, 139.66, 138.10, 136.13, 133.33, 133.23, 128.94, 128.59, 128.51, 128.40, 126.56, 126.48, 126.40, 126.20, 125.00, 123.16, 123.07, 121.52, 62.90, 54.47, 49.08, 48.62, 46.70, 20.52.

MS:- *m/z* 486 (M^+), 105.

Elemental analysis calculated for $C_{33}H_{26}O_4$:- C: 81.47, H: 5.38.

Found:- C: 81.48, H: 5.38.

3.5.4.4.4. Reaction of *N*-((Anthracen-9-yl)methyl)-1,2,3,4-tetrahydroisoquinoline (12f) with DMAD (13a).

In refluxing acetic acid, a 0.031 M solution of **12f** on treatment with 2 equivalents of **13a** for 6h gave a mixture of **14** (traces), **15** (traces), **8** (2%), **35** (41%) and **36** (10%).

In a repeat run, a 0.16 M solution of **12f** with 3 equivalents of **13a** for 4h gave a mixture of **14** (traces), **15** (traces), **8** (2%), **35** (13%), **36** (6%) and **38** (33%).

3.5.4.4.5. Reaction of *N*-((Anthracen-9-yl)methyl)-1,2,3,4-tetrahydroisoquinoline (12f) with DBA (13b).

In refluxing acetic acid, a 0.031 M solution of **12f** on treatment with 2 equivalents of **13b** for 6h gave a mixture of **14** (traces), **15** (traces), **8** (2%), **35** (43%) and **37** (15%).

In a repeat run, a 0.16 M solution of **12f** with 3 equivalents of **13b** for 4h gave a mixture of **14** (traces), **15** (traces), **8** (3%), **35** (15%), **37** (12%) and **39** (34%).

3.5.4.4.6. Reaction of *N*-((Anthracen-9-yl)methyl)-1,2,3,4-tetrahydroquinoline (12g) with DMAD (13a).

In refluxing acetic acid, a 0.031 M solution of **12g** on treatment with 2 equivalents of **13a** for 4h gave a mixture of **14** (traces), **15** (traces), **8** (4%), **35** (38%) and **36** (11%).

In a repeat run, a 0.16 M solution of **12g** with 3 equivalents of **13a** for 3h gave a mixture of **14** (traces), **15** (traces), **8** (3%), **35** (13%), **36** (4%) and **38** (38%).

3.5.4.4.7. Reaction of *N*-((Anthracen-9-yl)methyl)-1,2,3,4-tetrahydroquinoline (12g) with DBA (13b).

In refluxing acetic acid, a 0.031 M solution of **12g** on treatment with 2 equivalents of **13b** for 3h gave a mixture of **14** (traces), **15** (traces), **8** (2%), **35** (41%) and **37** (13%).

In a repeat run, a 0.16 M solution of **12g** with 3 equivalents of **13b** for 2h gave a mixture of **14** (traces), **15** (traces), **8** (3%), **35** (13%), **37** (10%) and **39** (36%).

3.5.4.4.8. Reaction of 9-(*N,N*-Bisanthracenemethyl)butylamine (12h) with DMAD (13a).

In refluxing acetic acid, a 0.022 M solution of **12h** on treatment with 2 equivalents of **13a** for 7h gave a mixture of **14** (traces), **15** (traces), **8** (3%), **35** (54%) and **36** (16%).

In a repeat run, a 0.11 M solution of **12h** with 3 equivalents of **13a** for 4h gave a mixture of **14** (traces), **15** (traces), **8** (2%), **35** (20%), **36** (10%) and **38** (38%).

3.5.4.4.9. Reaction of 9-(*N,N*-Bisanthracenemethyl)butylamine (12h) with DBA (13b).

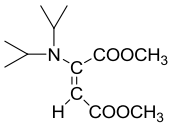
In refluxing acetic acid, a 0.022 M solution of **12h** on treatment with 2 equivalents of **13b** for 7h gave a mixture of **14** (traces), **15** (traces), **8** (3%), **35** (57%) and **37** (13%).

In a repeat run, a 0.11 M solution of **12h** with 3 equivalents of **13b** for 5h gave a mixture of **14** (traces), **15** (traces), **8** (2%), **35** (21%), **37** (12%) and **39** (39%).

3.5.4.5. Common Procedure for the Synthesis of Michael Adducts

A mixture of secondary amine (4 mmol) and dienophile (4 mmol) in 10 mL of DCM was stirred for about 10 minutes at RT. Progress of the reaction was monitored by TLC. When the reaction was complete, solvent was removed under reduced pressure. The Michael adduct obtained was purified by passing through a silica gel plug using hexane-DCM mixture.

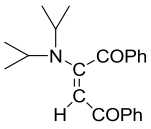
Compound 25a:-



Yield:- 95%

mp:- 93-95 °C.

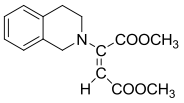
Compound 25b:-



Yield:- 94%

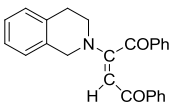
mp:- 115-117 °C.

Compound 34a:-



Yield:- 94%

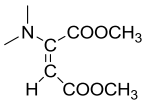
Compound 34b:-



Yield:- 94%

mp:- 64-66 °C.

Compound 41a:-



Yield:- 94%

mp:- 54-56 °C.

IR ν_{max} (KBr):- 1740, 1683 cm^{-1} (C=O stretch), 1244 cm^{-1} (C-O stretch).

^{1}H NMR ($CDCl_3$):- 4.59 (s, 1H), 3.94 (s, 3H), 3.64 (s, 3H), 2.88 (s, 6H).

^{13}C NMR ($CDCl_3$):- δ 168.11, 166.10, 155.18, 84.60, 52.92, 50.75, 39.75.

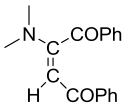
MS:- *m/z* 187 (M^+), 156, 128.

Elemental analysis calculated for

$C_8H_{13}NO_4$:- C: 51.31, H: 7.00, N: 7.48.

Found:- C: 51.30, H: 7.01, N: 7.49.

Compound 41b:-



Yield:- 94%

mp:- 84-86 °C.

IR ν_{max} (KBr):- 1652, 1596 cm^{-1} (C=Ostretch).

^{1}H NMR ($CDCl_3$):- 7.27-8.13 (m, 10H), 5.91 (s, 1H), 2.96 (br s, 6H).

^{13}C NMR ($CDCl_3$):- δ 186.20, 176.56, 135.86, 135.16, 129.81, 128.98, 128.92, 128.12, 127.72, 93.00, 40.14.

MS:- *m/z* 279 (M^+), 234, 105, 77.

Elemental analysis calculated for

$C_{18}H_{17}NO_2$:- C: 77.38, H: 6.14, N: 5.02.

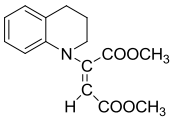
Found:- C: 77.39, H: 6.15, N: 5.00.

Compound 42a:-

Yield:- 92%

IR ν_{max} (KBr):- 1741, 1702 cm^{-1} (C=O stretch), 1147 (C-O stretch).

^{1}H NMR ($CDCl_3$):- 7.00-7.14 (m, 4H), 5.29 (s, 1H), 3.78 (s, 3H), 3.67 (s, 3H), 3.47 (t, 2H, *J* = 6.6 Hz),



2.71 (t, 2H, *J* = 6.2 Hz), 1.99 (quin, 2H, *J* = 6.4 Hz).

^{13}C NMR ($CDCl_3$):- δ 167.61, 165.75, 152.33, 139.58, 132.60, 128.50, 126.57, 124.58, 122.09, 93.65, 52.73, 51.09, 48.72, 26.83, 24.14.

MS:- *m/z* 275 (M^+).

Elemental analysis calculated for

$C_{15}H_{17}NO_4$:- C: 65.44, H: 6.22, N: 5.09.

Found:- C: 65.43, H: 6.23, N: 5.09.

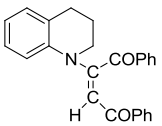
Compound 42b:-

Yield:- 92%

mp:- 68-70 °C.

IR ν_{max} (KBr):- 1678, 1617 cm^{-1} (C=O stretch).

^{1}H NMR ($CDCl_3$):- 7.04-8.03 (m, 14H), 6.67 (s, 1H), 3.54 (t, 2H, *J* = 6.2 Hz), 2.74 (t, 2H, *J* = 6.6 Hz), 1.99 (quin, *J* = 6.4 Hz).



^{13}C NMR ($CDCl_3$):- δ 193.78, 187.74, 158.98, 139.58, 138.84, 136.21, 133.20, 132.71, 131.69, 129.20, 128.75, 128.19, 128.14, 127.90, 126.31, 125.35, 124.22, 99.47, 48.35, 26.43, 23.96.

MS:- *m/z* 279 (M^+), 234, 105, 77.

Elemental analysis calculated for

$C_{25}H_{21}NO_2$:- C: 81.72, H: 5.76, N: 3.81.

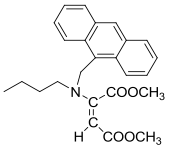
Found:- C: 81.71, H: 5.76, N: 3.81.

Compound 43a:-

Yield:- 93%

IR ν_{max} (KBr):- 1739, 1692 cm^{-1} (C=O stretch), 1155 cm^{-1} (C-O stretch).

^{1}H NMR ($CDCl_3$):- 7.25-8.28 (m, 9H), 4.99 (s, 2H), 4.78 (s, 1H), 3.78 (s, 3H), 3.50 (s, 3H), 2.38 (t, 2H, *J* = 8.2 Hz), 1.00-1.04 (m, 2H), 0.44-0.54 (m, 2H), 0.16 (t, 3H, *J* = 7.4 Hz).



^{13}C NMR ($CDCl_3$):- δ 168.43, 166.34, 154.87, 131.48, 131.29, 129.33, 129.16, 127.06, 125.25, 124.89, 123.61, 85.40, 52.96, 50.90, 47.19, 45.77, 19.56, 13.06.

MS:- *m/z* 405 (M^+), 191.

Elemental analysis calculated for

$C_{25}H_{27}NO_4$:- C: 74.03, H: 6.72, N: 3.46.

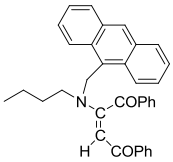
Found:- C: 74.04, H: 6.71, N: 3.47.

Compound 43b:-

Yield:- 92%

mp:- 135-137 °C.

IR ν_{max} (KBr):- 1682, 1619 cm^{-1} (C=O stretch).



^{1}H NMR ($CDCl_3$):- 7.36-8.51 (m, 19H), 6.50 (br s, 1H), 5.58 (br s, 1H), 2.47-2.74 (br, 2H), 1.32-1.47 (br, 2H), 0.73 (br, 2H), 0.36 (br, 3H).

^{13}C NMR ($CDCl_3$):- δ 186.88, 139.35, 135.98, 131.36, 131.31, 129.47, 129.31, 128.90, 128.36, 128.17, 127.79, 127.06, 125.29, 124.88, 123.61, 93.70, 19.60, 12.96.

MS:- *m/z* 497 (M^+), 105.

Elemental analysis calculated for

$C_{35}H_{31}NO_2$:- C: 84.47, H: 6.28, N: 2.82.

Found:- C: 84.48, H: 6.29, N: 2.81.

3.5.4.6. Common Procedure for the Reaction of Michael Adducts in Acetic Acid

a. With dienophile:-

A solution of Michael adduct (1.5 mmol) was refluxed with dienophile (3 mmol) in acetic acid and the progress of the reaction was monitored by TLC. When the reaction was complete, the reaction mixture was washed with a saturated solution of sodium bicarbonate and extracted with DCM. Organic extracts were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. If there were products other than polymeric material, they were purified by column chromatography on silica gel.

We could isolate the products **15**, **8** and **35** only from the decomposition reaction of **43a**. We could not isolate any products from the decomposition of Michael adducts **25a**, **34a** and **41-42a**. Decomposition of Michael adducts **25b**, **34b** and **41-42b,** however**,** yielded **37**. On the other hand, **43b** gave **37** along with **15**, **8** and **35**.

b. Without dienophile:-

A solution of Michael adduct (1.5 mmol) was refluxed in acetic acid and the progress of the reaction was monitored by TLC. The rate of the reaction was very slow compared to the above

reactions. After 10h, the reaction mixture was washed with a saturated solution of sodium bicarbonate and extracted with DCM. Organic extracts were combined, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. If there were products other than the reactant and polymeric material, they were purified by column chromatography on silica gel. This reaction was repeated under RT to reduce the polymerization.

Decomposition of Michael adducts without dienophile yielded the same products as in the reaction with dienophile. Only the rates of the reactions are different and hence the product yield.

3.6. References

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CHAPTER 4

PHOTOINDUCED ELECTRON TRANSFER REACTIONS OF (ANTHRACEN-9-YL)METHANAMINES

4.1. Abstract

Analysis of absorption and fluorescence emission spectra of (anthracen-9-yl)methanamines indicated intramolecular photoinduced electron transfer reactions leading to quenching of excited states, efficiency of which depends on the geometrical constraints and electronic factors pertaining to the molecule. Upon irradiation, (anthracen-9-yl)methanamines undergo intramolecular photoinduced electron transfer reactions to give multitude of products. In this chapter we explore the photoinduced electron transfer reactions of (anthracen-9-yl)methanamines, its mechanism and thereby build up a relation between the rate of the reaction, free energy change and quenching of excited states. Also we have studied the effect of solvents in the photoinduced electron transfer reactions of (anthracen-9-yl)methanamines.

4.2. Introduction

In 1866, J. Fritzache discovered the photoreaction of anth-

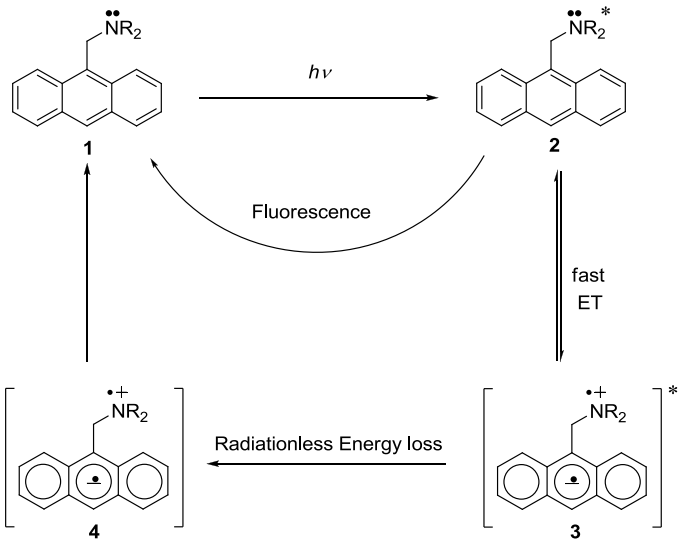
-racene and after several years the structure of the dimer was established.[1] Photochemical reactions of many easily available substituted anthracenes were investigated between 1955 and 1965 in order to establish the scope of dimerization. Also the research was focused on the structure and stereochemistry of the photoproducts.[2-5] Geometry of the photodimer depends on electronic and conformational factors.[6-9] Several reports on the mechanism of anthracene dimerization and anthracene fluorescence and phosphorescence are available in literature.[10-14] There are many reviews[15-17] on electronically excited anthracenes, such as the formation of intramolecular exciplexes, twisted intramolecular charge transfer (TICT) states, adiabatic cycloreversions and rotational isomerism in anthrylsubstituted ethylenes.

Nowadays photoresponsive supramolecular systems are of great interest due to their application in light-directed ionic switches, photoreversible cation traps, nanoscale devices for cation detection, light energy devices, etc.[18,19] Photoinduced electron transfer (PET) in 'donor-acceptor' molecules was mainly focused on the study of such photoresponsive systems.[20,21] These 'donor-acceptor' molecules are also used as p*H* indicators[22,23] and as sensors in biological[24] as well as in chemical[25] fields.

The photoinduced electron transfer process in a fluid medium which includes different steps[26-28] *viz* formation of the encounter complex, collision complex, contact ion pairs, solvent separated ion pairs, and free-radical ion pairs, is reversible. When forward electron transfer processes compete efficiently with the

energy wasting back-electron transfer processes, free radicals are generated in good yields.[29]

Amines are known quenchers of arene fluorescence by electron transfer.[30-32] We reasoned that quenching efficiency can further be improved by facilitating intramolecular electron transfer. Anthracenemethanamines are ideal substrates for exploring this possibility. Proposed mechanism of PET quenching for inbuilt amine-appended arene unit is explained in Scheme **4.1**.[33] Formation of intramolecular exciplex **3** can be seen in inbuilt amine-appended arene **1**. The short lived intramolecular exciplex **3** is formed by intramolecular single electron transfer from the locally excited amine-appended arene unit **2** and both are in equilibrium with each other. This is followed by radiationless energy loss to form an internal radical ion pair **4**. Back electron transfer taking place in the internal radical ion pair regenerates the ground state of **1**. Redox potential of the donor acceptor pair can be correlated with the quenching of fluorescence by electron transfer.



Scheme 4.1

Efficiency of intramolecular fluorescence quenching *via* PET depends on the spacer length[26,33,34] between donor and acceptor and the p*H* of the reaction medium.[23] Increasing both spacer length and p*H* of the medium will decrease intramolecular fluorescence quenching *via* PET.

It has already been reported that 9-(*N*,*N*-dimethylaminomethyl)anthracene undergoes photoinduced dimerization by irradiation in the solid state.[35,36] Irradiation of the salt formed by the reaction of 9-(*N*,*N*-dimethylaminomethy)anthracene with carboxylic acids in the solid state yielded different types of dimers and oxidized products. The products formed depend on the carboxylic acid coordinated to the amine.

In the present study, we have synthesised several (anthracen-9-yl)methanamines incorporating amine-arene unit having different electronic and steric environment around the nitrogen atom. In this chapter, we describe the solution phase steady state irradiation of (anthracen-9-yl)methanamines, product identification and elucidating plausible mechanism for the reactions. Earlier studies from our group[37] on intramolecular PET quenching of these (anthracen-9-yl)methanamines keeping 9-methylanthracene as reference helped us to develop a relation between percentage of fluorescence quenching by intramolecular PET and photochemical reaction rate.

4.3. Results and Discussion

We synthesised several (anthracen-9-yl)methanamines **5a-h** (Chart **4.1)** having different steric and electronic environment around the nitrogen atom. These were synthesized with a view to examining the effect of both steric and electronic environment around nitrogen on their photochemistry and photophysics.

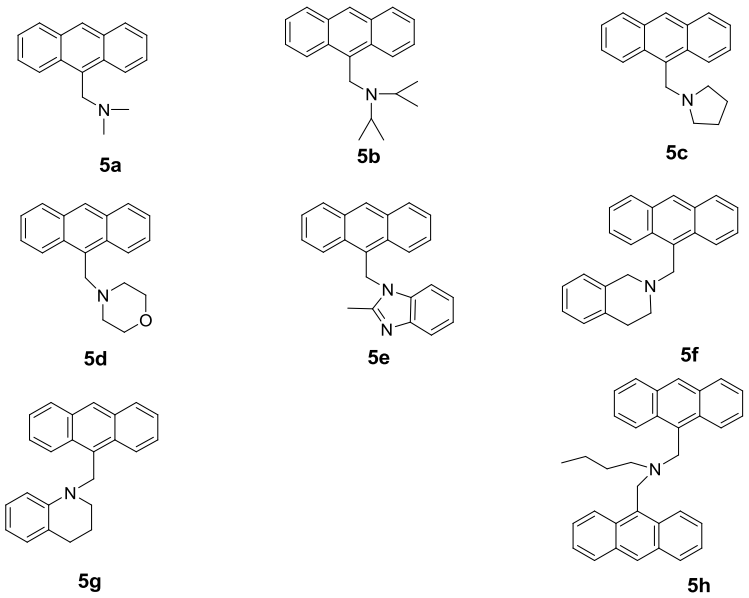
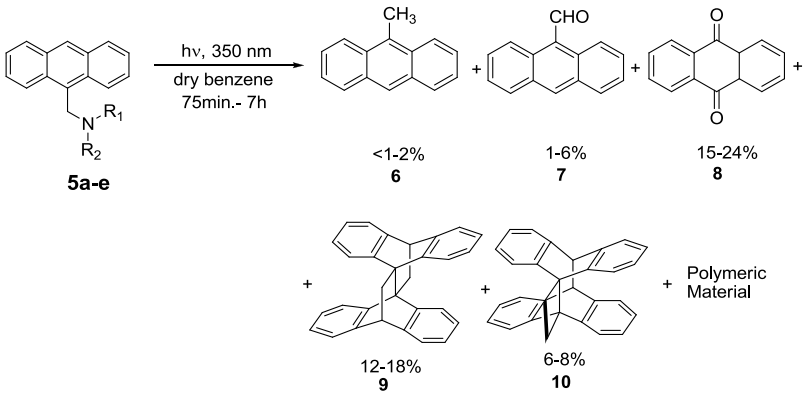


Chart 4.1

We irradiated a 1 mM solution of **5a** in dry benzene under argon atmosphere using 350 nm lamps. The reaction was completed in 7h and products obtained were separated, purified and characterised. 9-methylanthracene (**6**), 9-anthraldehyde (**7**), 9,10-anthraquinone (**8**), lepidopterene (**9**) and biplanene[38-40] (**10**) are the products formed in the photolysis of **5a**. To analyse the effect of steric and electronic effect around the nitrogen atom on the photoinduced electron transfer reactions of (anthracen-9-yl)methanamines, we have carefully studied the photoreactions of **5b-e** by supplying the same conditions as in the reaction of **5a**. All the reactions gave same products in near-identical yields as in the case of **5a** (Scheme **4.2**).



Scheme 4.2

However, reaction time varied from substrate to substrate. Based on these results, we concluded that though the mechanism of product formation is identical for **5a-e**, steric and electronic effect around the nitrogen atom do play a role in controlling rate of the overall chemical reaction. While **5b** and **5d** reacted very fast, **5c** exhibited reactivity comparable to that of **5a**. Imidazole appended anthracenemethanamine **5e** on the other hand reacted at a much slower rate and even after irradiating for 10h, appreciable amount of **5e** remained unchanged.

Based on results presented in Chapter 3 of this thesis, we conclude that anthracenemethyl radical is involved as an intermediate in the photochemical transformations of **5a-e**. Products such as **6**, **9** and **10** share common parentage of anthracenemethyl radical generated through electron transfer processes (*vide infra*). If this is true, rate of the photoreaction may depend on the electronic and steric effects around the nitrogen atom of (anthracen-9-yl)methanamines. An attractive proposal is that

electronic and steric environment around nitrogen control back electron transfer. In systems where back electron transfer is inefficient, higher reactivity is anticipated. However, this argument is somewhat superficial since the identity of rate determining step is uncertain. In order to shed more light on the observed variation in reactivity, we reexamined the photophysical behaviour of these compounds.

Our group has already studied the photophysical properties of (anthracen-9-yl)methanamines **5a-e**.[37] Photophysical studies unveiled the substituent effect on the fluorescence emission spectra of **5a-e**. Fluorescence emission of **5a-e** showed a slight red shift (1-7 nm) in comparison with 9-methylanthracene due to substituent effects. Quenching of anthracene fluorescence (28-99%) was observed in **5a-e**. Compound **5d** showed high efficiency in quenching (99%). This was followed by **5a** (94%), **5b** and **5c** (90% each). Among the series, as expected, **5e** showed least efficiency (28%) in quenching of anthracene fluorescence. This result clearly indicates differential rates of photoinduced electron transfer in these compounds. We infer that efficiency of electron transfer from the amine lone pair to the anthracene component largely depends on the steric deformations of the amine nonbonding orbital.

Compound **5a-d** have alkyl amine components and exhibit higher quenching capability. In the case of **5e**, electron pair on nitrogen is part of an aromatic ring system and hence is less available for PET process. Consequently, **5e** shows the least magnitude of fluorescence quenching of anthracene fluorophore *via*

PET in the **5a-e** series. In other words, as availability of lone pair electron decreases the quenching capability also decreases. 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 using Rehm-Weller equation.[34,37,41-42] Change in free energy is higher when the quenching efficiency is lower. The higher quenching of **5d** may be due to the powerful interaction of oxygen atom in the excited state.

From the results obtained by the photophysical and photochemical studies of (anthracen-9-yl)methanamines **5a-e**, we can correlate rate of the reaction, percentage of fluorescence quenching and change in free energy (Chart **4.2**). Compounds with high percentage of fluorescence quenching have higher reaction rate and change in free energy for these systems is below -10 kcal/mol. However, direct correlation of reaction rate with efficiency of fluorescence quenching is risky. Efficiency of back electron transfer is equally or, may be, more important in controlling reaction rates (*vide infra*)

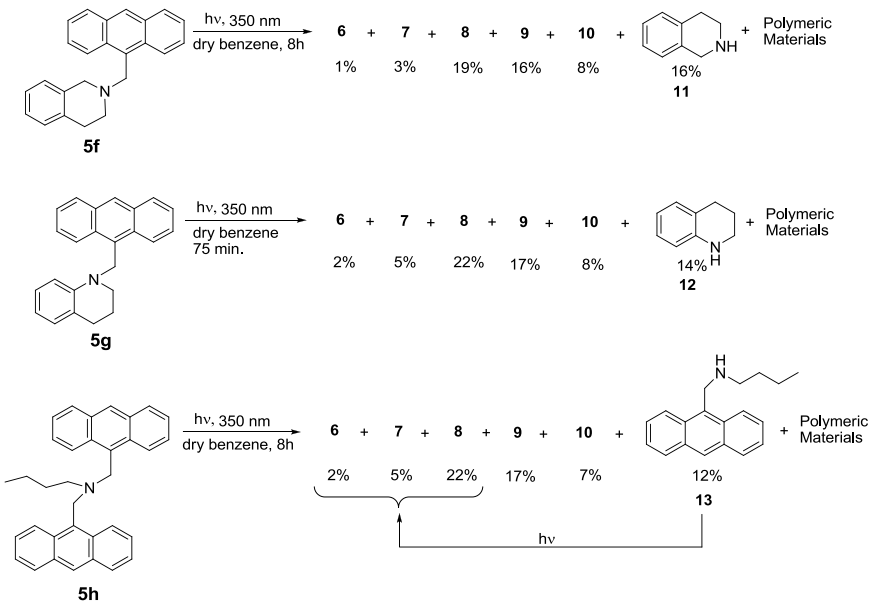
(Anthracen-9-yl)methanamines	Percentage of Fluorescence Quenching (compared to 9-methylanthracene)	Change in Free Energy (kcal/mol)	Time Taken for the Complete Removal of Starting Material
5a	90	-14.71	7h
5b	94	-10.09	90min.
5c	90	-9.87	7h
5d	99	-15.17	75min.
5e	28	-1.83	>10h

Chart 4.2

In the photolysis of the (anthracen-9-yl)methanamines **5a-d** we could not establish the fate of amine component in these reactions presumably due to loss of amine component as volatile fractions that could not even be detected by GC-MS analysis. This proved to be major roadblock for us since without dependable information on the fate of amine component, it is not feasible to establish the mechanism for the observed photoreactions of anthracenemethanamines. Since the rate of the reaction of **5e** is very low compared to other (anthracen-9-yl)methanamines, formation of amine component is very low. Nevertheless, traces of 2-methylimidazole (the amine component) could be detected by GC-MS analysis. To fortify this result we selected (anthracen-9-yl)methanamines having high fluorescence quenching and significant amine component. So we repeated the reaction using (anthracen-9-yl)methanamines having significant amine component **5f-h**.

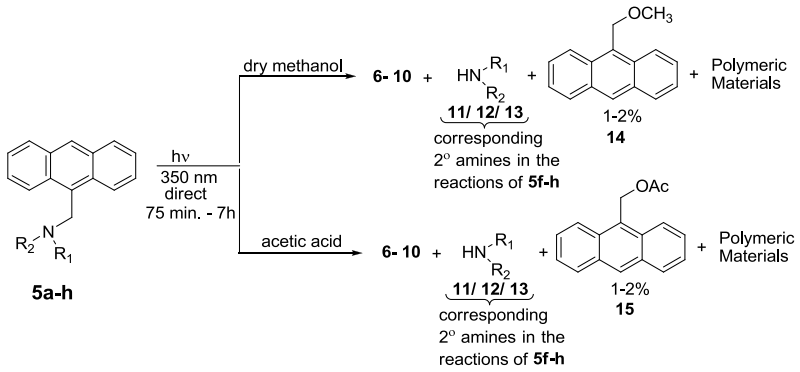
Amine components could be easily traced out from the photoreactions of **5f-h**. Thus, irradiation of **5f** gave significant amounts of 1,2,3,4-tetrahydroisoquinoline (**11**). Similarly, **5g** gave 1,2,3,4-tetrahydroquinoline (**12**) and **5h** gave *N*-butylanthracenemethanamine (**13**). Surprisingly, rate of the reaction of **5g** is higher than that of **5f** and **5h**, only 75minutes is required for the complete reaction of **5g** whereas **5f** and **5h** requires 8h each (Scheme **4.3**). On the basis of electron availability on nitrogen, one would have expected lower efficiency for electron transfer in the case of **5g** thanks to efficient delocalization of lone pair electrons

on nitrogen. However, it may be noted that radical cation centre once generated in **5g** is stabilized by resonance and hence back electron transfer in this case is not exigent. In retrospect, similar suppression in back electron transfer in **5d** having morpholine component may be attributable to fast photochemical reaction exhibited by it. Electron hopping from ring oxygen to the radical cation centre on nitrogen is a distinct possibility here. In other words, in anthracenemethanmines where either excited state electron transfer from nitrogen to anthracene component is very efficient or back electron transfer is less prominent are the ones that react faster.



Scheme 4.3

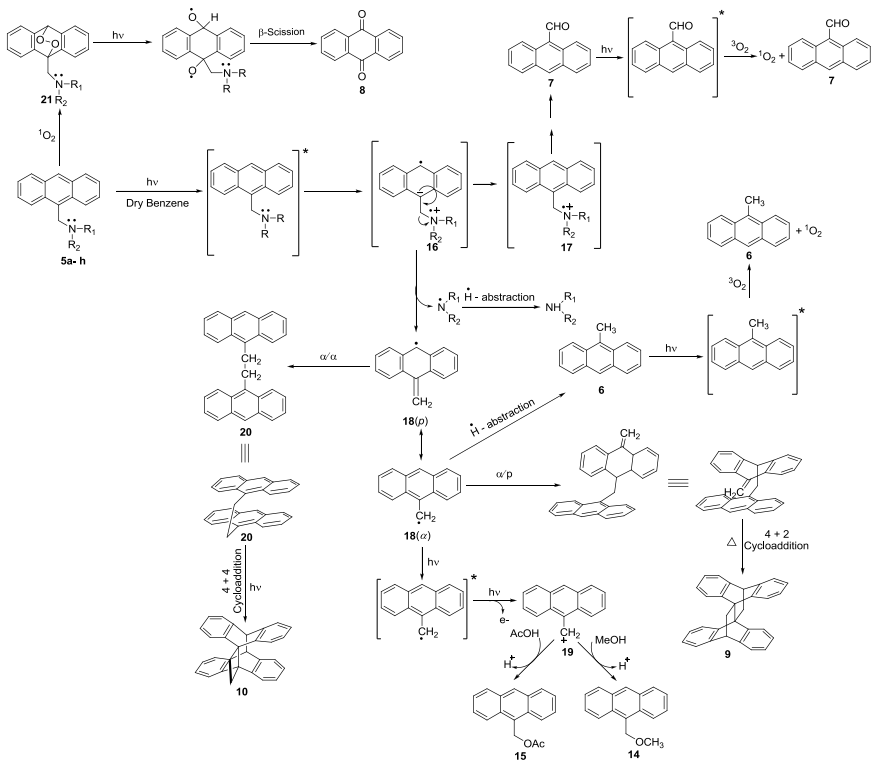
To study the effect of solvent dependency in the photochemical reaction, we have the photoreaction of (anthracen-9-yl)methanamines **5a-h** in polar protic media-alcohol (methanol) and acid (acetic acid). Here the reaction rate was similar to that of the photoreaction in nonpolar solvent-benzene. In the photoreaction in methanol, 9-(methoxymethyl)anthracene[43] (**14**) and in acetic acid yielded (anthracen-9-yl)methyl acetate[43] (**15**) in addition to the above products in Schemes **4.2** and **4.3** (Scheme **4.4**) were generated. Formation of **14** and **15** alludes to the generation of anthracenemethyl cation as an intermediate in irradiation carried out in methanol and acetic acid. Generation of anthracenmethyl cation is explained in terms of a biphotonic pathway involving further excitation of initially formed anthracenemethyl radical. Similar multiple-photon chemistry has been observed in the laser-jet photolysis of 9-(phenoxymethyl)anthracene and 9,10-bis-(phenoxymethyl)anthracene.[40] Furthermore, generation of secondary amine products is indicative of the generation of aminium radical intermediate.



Scheme 4.4

Mechanism of the photochemical reaction of (anthracen-9-yl)methanamines **5a-h** can be explained by the intramolecular one electron transfer which takes place in (anthracen-9-yl)methanamines by irradiation to form an intramolecular aminium radical cation-anthraceneradical anion pair **16**. This leads to the destabilization and cleavage of C-N bond to form 9-*p*-methylanthracene radical (**13*(p)***) and aminium radical. Radical **13*(p)*** exists in equilibrium with α form of 9-methylanthracene radical **13*(α)***. Hydrogen atom abstraction by 9-α-methylanthracene radical and aminium radical gave 9-methylanthracene (**6**) and corresponding secondary amine respectively. Generation of anthraldehyde (**7**) on the basis of the generation of anthracenemethanamine radical cation **17** from **16** followed by loss of hydrogen atom from α-carbon to form iminium ion and subsequent hydrolysis. Lepidopterene (**9**) was formed by the α/p dimerization of **13** followed by intramolecular [4+2] cycloaddition. This is a thermal intramolecular cycloaddition, a facile process even at room temperature.[44] Biplanene (**10**) was formed by the α/α dimerization of **13** to form 1,2-bis(9-anthracenyl)ethane (**20**) followed by intramolecular [4+4] cycloaddition. In reactions done in polar solvents, photoionization of 9-α-methylanthracene radical generate 9-anthracenemethyl cation (**19**) that is subsequently trapped by methanol and acetic acid to produce **14** and **15** respectively. 9,10-anthraquinone (**8**) was formed through the homolysis followed by β-scission of the endoperoxide **21** of **5a-h**, which is formed by the reaction of singlet oxygen with **5a-h**.[45]

Singlet oxygen, probably, is formed by the photoreaction of **6** and **7** with triplet oxygen (Scheme **4.5**).



Scheme 4.5

4.4. Conclusion

We have studied the photochemical transformation of (anthracen-9-yl)methanamines by characterising the products formed and have proposed plausible mechanisms to account for the observed transformations. In addition, we have built a relation between percentage of fluorescence quenching, change in free

energy and reaction rate. As (anthracen-9-yl)methanamines show high percentage of fluorescence quenching, they have higher reaction rate and lower value of change in free energy. By doing the photoreaction in methanol and acetic acid, we can see the solvent dependency in the photoinduced electron transfer reactions of (anthracen-9-yl)methanamines.

4.5. Experimental

4.5.1. General Techniques

All reactions were carried out using oven dried glasswares. All experiments were done with distilled and dried solvents by using standard protocols. All starting materials were purchased from either *Sigma-Aldrich* or *Spectrochem Chemicals* and were used without further purification. Progress of the reaction and chromatographic separations were monitored by dried and activated silica gel TLC plates (Aluminium sheets coated with silica gel, *E. Merck*). Visualisation of TLC plates was acquired by exposure to iodine vapours or UV lamp. Separation and purification of compounds were done by column chromatography using either silica gel (*Spectrochem Chemicals*, 60-120 mesh) or neutral alumina (*Spectrochem Chemicals)*. The products were further purified by recrystallization from suitable solvent systems. Solvent eluted from the column chromatography was concentrated using *Heidolph* rotary evaporator. Melting points are uncorrected

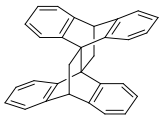
and were determined on a *Neolab* melting point apparatus. Infra-red spectra were recorded using *Jasco 4100* and *ABB Bomem (MB Series)* FT-IR spectrometers. The ^{1}H NMR spectra were recorded at 400 MHz FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS. Elemental analysis was performed using *Elementar Systeme (Vario EL III)*. Molecular mass was determined by electron impact (EI) method using GC-MS (*Agilent GC-7890A, Mass-5975C*) and fast atom bombardment (FAB) using *JMS 600 JEOL* mass spectrometer. Here we are giving the spectral and analytical data only for novel compounds and the corresponding reference cited for known compounds.

4.5.2. Common Procedure for Photochemical Irradiation

A degassed solution of (anthracen-9-yl)methanamines (1 mmol) in dry benzene or dry methanol or acetic acid was irradiated under argon atmosphere using 350 nm lamps. The progress of the reaction was monitored by TLC. Benzene was removed under reduced pressure and the residue was chromatographed over silica gel. Elution with hexane gave **6** and **7** was obtained by the elution using a mixture of (4:1) hexane and dichloromethane. Compounds **9** and **10** are obtained by the elution using (7:3) hexane and dichloromethane. Elution with a mixture of (3:2) hexane and dichloromethane yielded **8**. The reaction time depends up on the nature of (anthracen-9-yl)methanamines and was indicated in each

scheme.

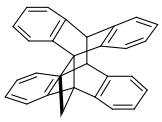
Compound 9[46]**:-**



mp:- 316-318 °C.

MS:- *m/z* 382 (M^+).

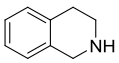
Compound 10[47]**:-**



mp:- 327-329 °C.

MS:- *m/z* 382 (M^+).

Compound 11[48]**:-**

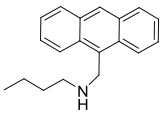


MS:- 133 (M^+).

Compound 12[49]**:-**

MS:- 133 (M^+).

Compound 13[50]**:-**



mp:- 38-40 °C.

MS:- *m/z* 263 (M^+), 191.

4.6. References

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CHAPTER 5

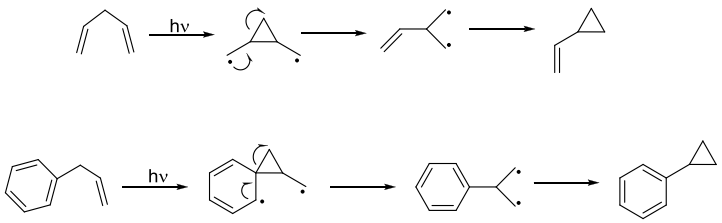
PHOTOCHEMICAL TRANSFORMATIONS OF 9-AMINOMETHYLANTHRACENE DERIVED DIBENZOBARRELENES AND BISDIBENZOBARRELENES

5.1. Abstract

Dibenzobarrelenes undergo photochemical transformation to give dibenzocyclooctatetraene and dibenzosemibullvalene respectively through singlet and triplet excited states. Tertiary amines are efficient quenchers of singlet-excited states. In this chapter we focus on the photoreactions of dibenzobarrelenes and bisdibenzobarrelenes with 'in built' singlet quenchers based on the assumption that tertiary amines quench singlet excited state of barrelenes by electron transfer process while leaving triplets to react freely. In the irradiation of amine appended dibenzobarrelenes, though singlet mediated cyclooctatetraene generation was completely suppressed, contrary to our expectation, triplet mediated semibullvalene formation was also not observed. Instead, these barrelenes underwent intramolecular electron transfer mediated retro Diels-Alder reaction.

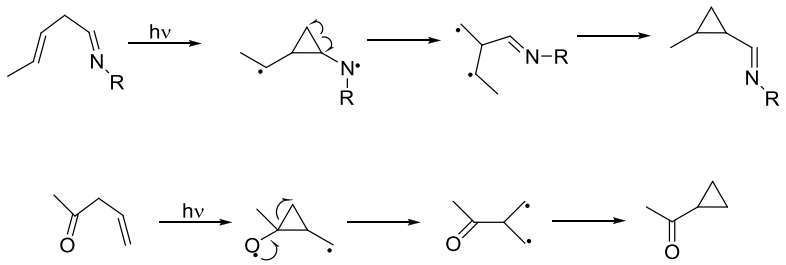
5.2. Introduction

Vinylcyclopropane formation in the photolysis of reactants having two vinyl moieties bonded to an sp^3 hybridized carbon is termed as di-π-methane rearrangement or Zimmerman rearrangement or divinylmethane rearrangement.[1] It was first reported independently by Zimmerman and Grunewald[2] in 1966 (Scheme **5.1**).



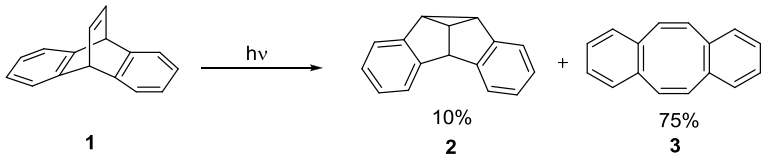
Scheme 5.1

Aza-di-π-methane rearrangement (ADPM) and oxa-di-π-methane rearrangement (ODPM) are the common variations of Zimmerman rearrangement.[3] In ADPM,[4-6] C=N serves as one of the π groups and one of the two π moieties is a carbonyl group in ODPM[7-10] (Scheme **5.2**).



Scheme 5.2

Dibenzobarrelene (**1**) undergoes photochemical transformation to give both dibenzosemibullvalene (**2**) and *sym*-dibenzocyclooctatetraene (**3**). Here **2** is formed by triplet-mediated di-π-methane rearrangement, **3** is formed by [2+2] photocycloaddition via the singlet excited state[11-13] (Scheme **5.3**).



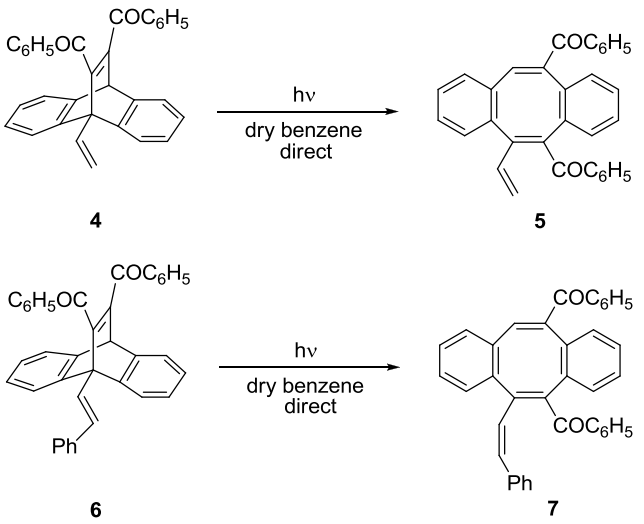
Scheme 5.3

Ciganek[11] first reported the effect of bridgehead substituents on the regioselectivity of di-π-methane rearrangement. Friedman[12] indicated the effect of electronic factors in the initial bonding in di-π-methane rearrangement. Iwamura,[14] Richards[15] and Scheffer[16-19] conducted detailed investigations on the effect of bridgehead substituents. Recently from our group, Mathew[20] constructed a clear picture on the effect of bridgehead substituents

in controlling the regioselectivity of di-π-methane rearrangement by detailed examination of several tethered barrelenes.

When barrelenes are irradiated in the presence of triplet sensitizer, semibullvalene is formed in high yield,[1] while cyclooctatetraene is formed by direct irradiation through pericyclic reactions via singlet excited state.[12] In practice, both singlet mediated cyclooctatetraene and triplet mediated semibullvalene are concurrently generated. The ratio at which these products are formed depends on several factors including adventitious impurities present in solvent and hence (the ratio) is difficult to predict. [21]

Our group has done a detailed study on improving the selectivity of photochemical transformation of barrelenes by controlling the competing pathways through intramolecular quenching.[22,23] Olefin moiety can efficiently quench the triplet excited state,[24,25] so we synthesized various bridgehead olefin appended dibenzobarrelenes. Irradiation of bridgehead olefin appended dibenzobarrelenes **4** & **6** selectively yielded singlet mediated dibenzocyclooctatetraene **5** & **7** by quenching the triplet excited state of the dibenzobarrelenes through the *cis-trans* isomerisation of the bridgehead olefin appendages (Scheme **5.4**). The efficiency of the intramolecular triplet quenching depends on the substituents on dibenzobarrelenes.[22]



Scheme 5.4

In the above reaction we can clearly observe that the olefins are efficiently quenching (intramolecularly) the triplet state and photoreaction of dibenzobarrelenes occurred exclusively through singlet state. This efficient selective quenching steered us to study the photochemical reaction of tertiary amine appended dibenzobarrelenes and bisdibenzobarrelenes. Tertiary amines are efficient quenchers of singlet excited states by electron transfer.[26,27] In Chapter 3, we have reported generation of dibenzobarrelenes and bisdibenzobarrelenes having 'in built' tertiary amine components. These 9-aminomethylanthracene derived dibenzobarrelenes and bisdibenzobarrelenes are used to study the effect of 'in built' singlet quencher in the photochemical transformation because intramolecular quenching of singlet excited states is more effective

since singlets are short lived than triplets and singlet excited states quenching may not be very efficient by collision limited intermolecular processes.

In this chapter we have examined the photochemistry of various tertiary amine appended dibenzobarrelenes and bisdibenzobarrelenes. We have characterised the products formed and proposed plausible mechanisms to account for the generation of various photoproducts.

5.3. Results and Discussion

Reaction of (anthracen-9-yl)methanamines with suitable electron deficient dienophiles such as DMAD and DBA in xylene or DMF yielded the corresponding 9-aminomethylanthracene derived dibenzobarrelenes and bisdibenzobarrelenes (Chart **5.1**).[28]

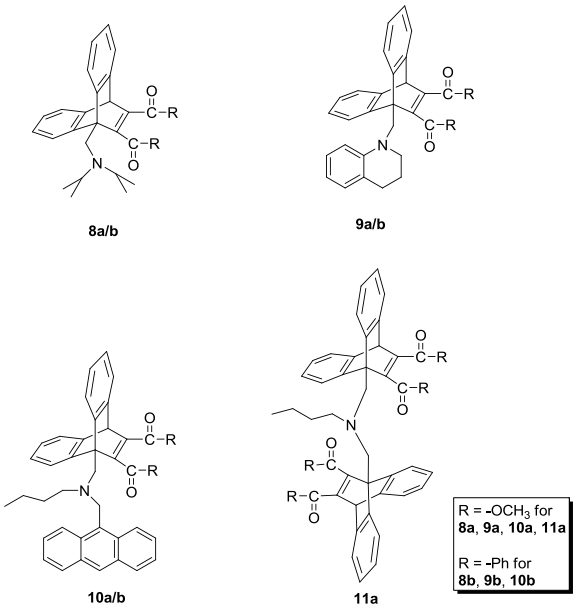
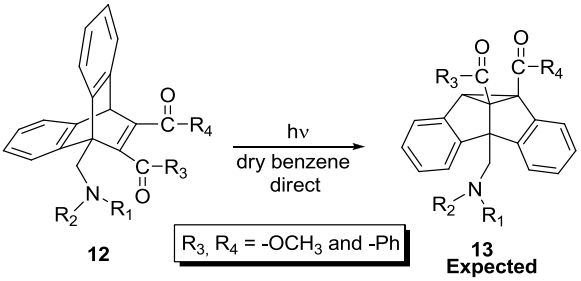


Chart 5.1

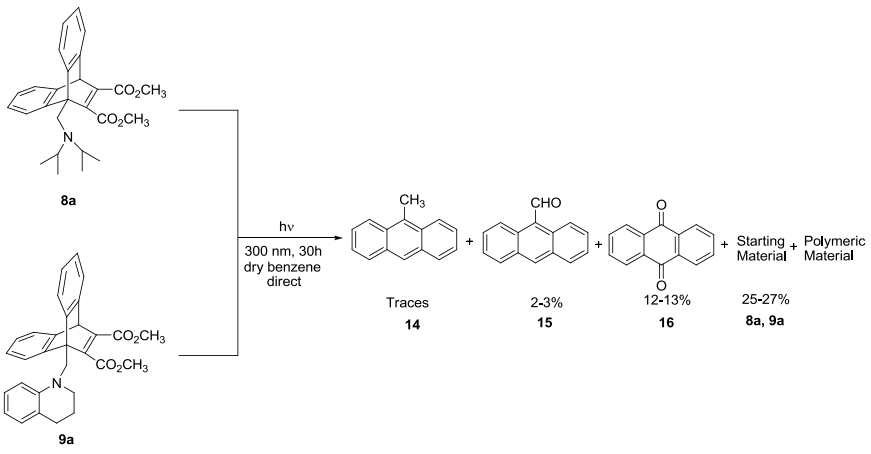
Since tertiary amines are efficient quenchers for singlet excited state, we expected the photoreaction amine appended dibenzobarrelenes **12** to proceed exclusively through triplet excited state to yield the corresponding dibenzosemibullvalenes **13** (Scheme **5.5**).



Scheme 5.5

Bisdibenzobarrelenes may photochemically react in the same way as above yielding the corresponding bisdibenzosemibullvalenes.

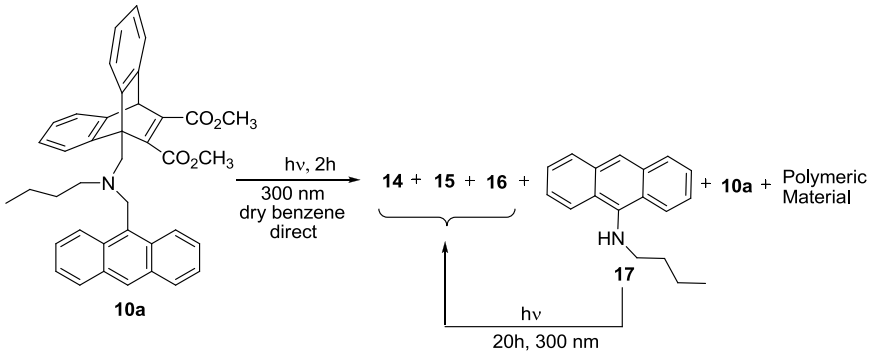
In order to examine quenching of singlet excited state in the photoreaction of barrelenes, we irradiated 0.8 mM solution of **8a** in dry benzene at 300 nm under argon atmosphere. Contrary to our expectation, semibullvalene was not formed in this reaction. Instead, fragmentation products such as 9-methylanthracene (**14**), 9-anthraldehyde (**15**) and 9,10-anthraquinone (**16**) were generated in low yield. Considerable amount of unchanged starting material along with some polymeric material could also be isolated. In order to examine the generality of the reaction, we carried out the irradiation of **9a** under conditions identical to those reported for **8a**. Here also the same products are obtained as in the above reaction in comparable yields (Scheme **5.6**). Interestingly products such as **14**, **15** and **16** are generated in the reaction between amine appended anthracenes and suitable electron acceptors.[28]



Scheme 5.6

So the photoreaction of tertiary amine appended dibenzobarrelenes is not influenced by the substituents on nitrogen atom.

In the photoreaction of **10a**, after 2h we could detect the presence of (*N*-butylaminomethyl)anthracene (**17**) along with **14**, **15** and **16**. However, concentration of **17** diminished with time. We conclude that **17** undergoes further reactions to give **14**, **15** and **16** (Scheme **5.7**).

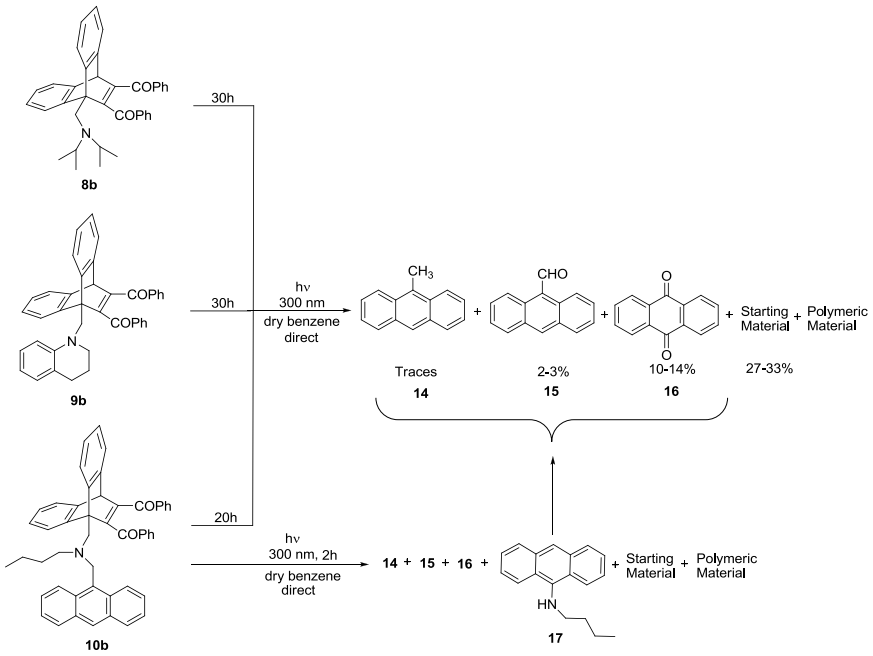


Scheme 5.7

In an earlier investigation we observed that, intramolecular quenching in quencher-appended dibenzobarrelenes are depending on the nature of substituents present in the barrlene chromophore. While efficient quenching of barrelene triplet was observed with olefin appended anthracene-DBA adducts, no quenching was observed in the case of olefin appended anthracene-DMAD adducts.[22]

In the light of the above mentioned possibility, we examined the photoreaction of **8b-10b** in dry benzene by supplying

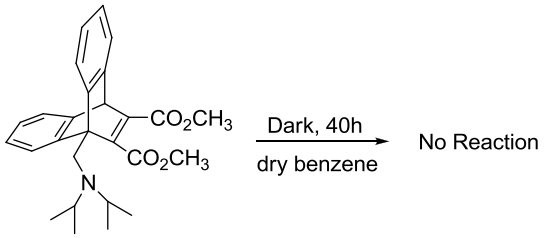
the same conditions as with **8a**/**9a**. We observed that **8b**-**10b** reacted identically with **8a**-**10a**. After 2h, as in the case of **10a**, we could detect the presence of (*N*-butylaminomethyl)anthracene (**17**) in the reaction of **10b** (Scheme **5.8**). Based on these results, we concluded that the photoreaction of tertiary amine appended dibenzobarrelenes is not affected by other substituents present on dibenzobarrelenes.



Scheme 5.8

In a control experiment, we conducted the reaction of **8a** in the absence of light to study the role of light in the above reactions. In the absence of light, even after 40h no new products were

formed and unchanged **8a** was isolated in near-quantitative amounts (Scheme **5.9**). Thus, generation of various products such as **14**, **15** and **16** is indeed through a photochemical pathway.



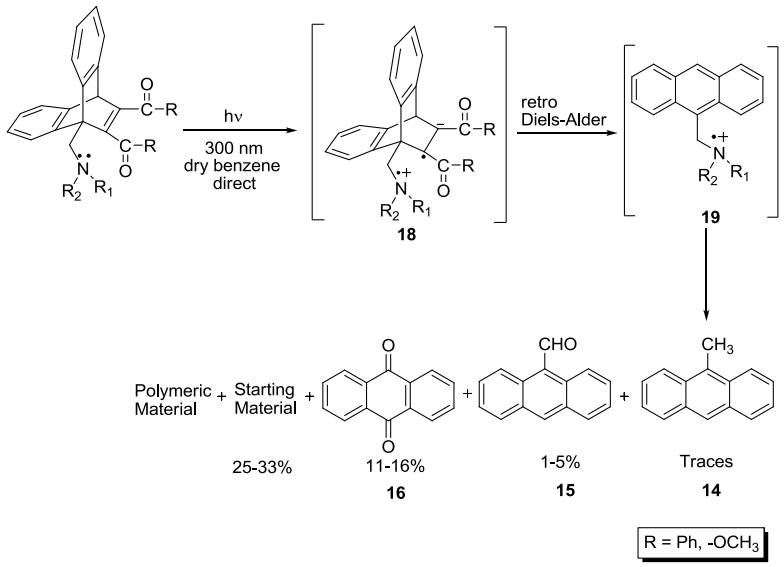
Scheme 5.9

As mentioned earlier, in the irradiation of **8a/b-10a/b**, some of the products formed are identical to those formed in the reaction between (anthracen-9-yl)methanamines and electron acceptors such as DMAD and DBA. We invoked anthracenemethyl radical as a possible intermediate in those reactions. Hence, anthracenemethyl radical is a possible intermediate in the photochemical reaction as well. This in turn suggests the generation of the radical cation of anthracenemethanamine through a retro Diels-Alder pathway. Interestingly, dimerization of anthracenemethyl radical was not observed under photochemical conditions. A conservative explanation is that anthracenemethyl radicals are generated under such low concentration where dimerization is not competitive.

Based on the results presented above, we propose the following mechanism for the photoreaction of amine appended

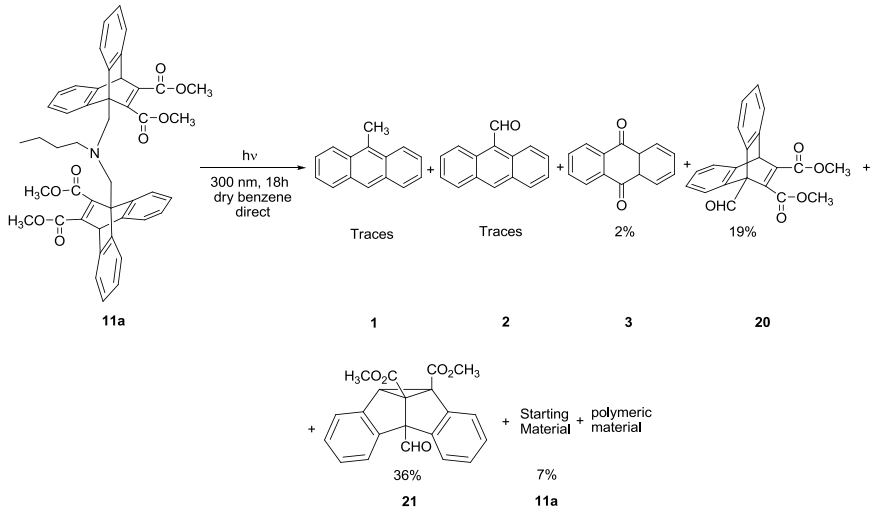
barrelenes **8a/b-10a/b**. Since the barrelene chromophore and amine components are isolated from each other by the methylene spacer, it may be assumed that in the excited state barrelene accepts an electron from the amine appendage. Ensuing retro Diels-Alder reaction results in the generation of anthracenemethanamine radical cation that undergoes further transformations as reported in previous chapters to give the products such as **14**, **15** and **16**.[29] Electron transfer mediated cycloreversion reactions are well documented in literature.[30-32]

When tertiary amine appended dibenzobarrelenes are photoexcited, intramolecular single electron transfer from the tertiary amine appendage to the excited state of barrelene chromophore results in the generation of radical anion-radical cation pair **18** that undergoes retro Diels-Alder reaction to form (anthracen-9-yl)methanamine radical cation **19** (Scheme **5.10**). This (anthracen-9-yl)methanamine radical cation **19** undergoes further reactions to give the products **14**, **15** and **16**. Detailed studies on the mechanism of the formation of above compounds are discussed in chapter 4.



Scheme 5.10

Photochemical transformation of bisdibenzobarrelene **11a** yielded **20** and **21** along with **14**, **15** and **16** (Scheme **5.11**). Here two new products **20** and **21** are formed in bisdibenzobarrelene photoreaction other than dibenzobarrelene photoreaction. Here also the reaction proceeded through electron transfer mediated retro Diels-Alder reaction. Intramolecular single electron transfer in **11a** leads to the formation of amine radical cation followed by the loss of a hydrogen atom from α-carbon atom to yield iminium ion which undergo hydrolysis to give **20**. The barrelene **20** undergoes di-π-methane rearrangement to yield **21**.[14] Other products **14**, **15** and **16** are formed by the same mechanism presented in Scheme **5.11**.



Scheme 5.11

5.4. Conclusion

We have examined the photochemistry of a few 9-aminomethylanthracene derived dibenzobarrelenes and a bisdibenzobarrelene. Since tertiary amines are efficient singlet quenchers, so we expect that the barrelenes having 'in built' singlet quencher may undergo photochemical transformation through triplet pathway by intramolecular singlet quenching. But the reaction of dibenzobarrelenes was proceeded through intramolecular electron transfer followed by retro Diels-Alder reaction to form the products through the intermediate (anthracen-9-yl)methanamine radical cation.

Bisdibenzobarrelene also shows the same reaction, but two

new products are formed other than dibenzobarrelene reactions. One of the new products is formed by single electron transfer reaction followed by hydrolysis and another is formed by its photoreaction by di-π-methane rearrangement.

5.5. Experimental

5.5.1. General Techniques

All reactions were carried out using oven dried glasswares. All experiments were done with distilled and dried solvents by using standard protocols. All starting materials were purchased from either *Sigma-Aldrich* or *Spectrochem Chemicals* and were used without further purification. Progress of the reaction and chromatographic separations were monitored by dried and activated silica gel TLC plates (Aluminium sheets coated with silica gel, *E. Merck*). Visualisation of TLC plates was acquired by exposure to iodine vapours or UV lamp. Separation and purification of compounds were done by column chromatography using either silica gel (*Spectrochem Chemicals*, 60-120 mesh) or neutral alumina (*Spectrochem Chemicals)*. The products were further purified by recrystallization from suitable solvent systems. Solvent eluted from the column chromatography was concentrated using *Heidolph* rotary evaporator. Melting points are uncorrected

and were determined on a *Neolab* melting point apparatus. Infra-red spectra were recorded using *Jasco 4100* and *ABB Bomem (MB Series)* FT-IR spectrometers. The ^{1}H NMR spectra were recorded at 400 MHz FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS. Elemental analysis was performed using *Elementar Systeme (Vario EL III)*. Molecular mass was determined by electron impact (EI) method using GC-MS (*Agilent GC-7890A, Mass-5975C*) and fast atom bombardment (FAB) using *JMS 600 JEOL* mass spectrometer. Here we are giving the spectral and analytical data only for novel compounds and the corresponding reference cited for known compounds.

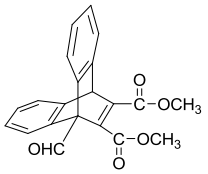
5.5.2. Common Procedure for Photochemical Irradiation

A degassed solution of 9-aminomethylanthracene derived dibenzobarrelenes **8a/b-10a/b** (0.8 mmol) in dry benzene was irradiated under argon atmosphere using 300 nm lamps. Progress of the reaction was monitored by TLC. Benzene was removed under reduced pressure and the residue was chromatographed over silica gel. Elution with hexane gave **14** and **15** was obtained by the elution using a mixture of (4:1) hexane and dichloromethane. Elution using a mixture of (3:2) of hexane and dichloromethane yielded **16**. The reaction time depended on the nature of dibenzobarrelenes and is indicated in each scheme.

Irradiation of 11a:-

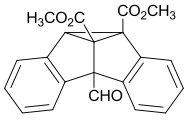
9-Aminomethylanthracene derived bisdibenzobarrelene **11a** (0.4 mmol) in dry benzene was irradiated under argon atmosphere using 300 nm lamps for 18h. Progress of the reaction was monitored by TLC. Benzene was removed under reduced pressure and the residue was chromatographed over silica gel. Elution with hexane gave **14** and **15** was obtained by the elution using a mixture of (4:1) hexane and dichloromethane. Elution using a mixture of (3:2) hexane and dichloromethane yielded **16**. Products **20** and **21** were obtained by the elution using a mixture (1:1) of hexane and dichloromethane.

Compound 20[33]:-



^{1}H NMR ($CDCl_3$):- 10.75 (s, 1H), 7.16-7.39 (m, 8H), 5.23 (s, 1H), 3.77 (s, 3H), 3.70 (s, 3H).

Compound 21[14]:-



^{1}H NMR ($CDCl_3$):- 10.11 (s, 1H), 6.99-7.31 (m, 8H), 4.49 (s, 1H), 3.82 (s, 3H), 3.66 (s, 3H).

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List of Poster Presentations

1. Photolytic oxidation of 9-aminomethylanthracene to anthraquinone, Jacob, J. P.; Mallia, R. R.; Unnikrishnan, P. A.; Manoj, N.; Prathapan, S. *International Conference on Materials for the Millennium (MatCon)*, **2010**.
2. Studies on the solvent dependence in the reaction of 9-(*N*,*N*-dimethylaminomethyl)anthracene with DMAD, Jacob, J. P.; Unnikrishnan, P. A.; Manoj, N.; Prathapan, S. *5th mid-year CRSI symposium,* **2010**.
3. Studies on the solvent dependence in the reaction of 9-(*N*,*N*-dimethylaminomethyl)anthracene with DBA, Jacob, J. P.; Mallia, R. R.; Unnikrishnan, P. A.; Manoj, N.; Prathapan, S. *Current Trends in Chemistry (Citric)*, **2011**.
4. Reaction of (anthracen-9-yl)methanamines with ceric ammonium nitrate, Ligi, M. L.; Jacob, J. P.; Unnikrishnan, P. A.; Manoj, N.; Prathapan, S. *Current Trends in Chemistry (Citric)*, **2012**.*

∗ Not a part of work presented in this thesis.