INVESTIGATIONS ON ELECTRON TRANSFER REACTIONS OF A FEW ANTHRACENEMETHYL SULFIDES WITH SUITABLE ELECTRON ACCEPTORS AND RELATED STUDIES

Thesis submitted to the
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Doctor of Philosophy

in

Chemistry

in the Faculty of Science
by

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under the supervision of

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December 2014

DECLARATION

I hereby declare that the work presented in the thesis entitled **"Investigations on electron transfer reactions of a few anthracenemethyl sulfides with suitable electron acceptors and related studies"** 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 **Reshma G.**

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CERTIFICATE

This is to certify that the thesis entitled **"Investigations on electron transfer reactions of a few anthracenemethyl sulfides with suitable electron acceptors and related studies"** is a genuine record of research work carried out by **Ms. Reshma G.**, under my supervision, in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry of Cochin University of Science and Technology, and further that no part thereof has been presented before for the award of any other degree. All the relevant corrections and modifications suggested by the audience and recommended by the doctoral committee of the candidate during the presynopsis seminar have been incorporated in the thesis.

Cochin-22
24-12-2014

Dr. Prathapan S.
(Supervising Guide)

Dedication

To my respected teachers, beloved family and friends for
always supporting, helping and standing by me.

"A man would do nothing if he waited until he could do it so
well that no one could find fault with what he has done."
– John Henry Newman

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*Above all, I thank **God Almighty** for His blessings.*

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PREFACE

At the heart of organic chemistry are fundamental concepts of molecular structure and reactivity of carbon containing compounds.
(Francis A. Carey and Richard J. Sundberg)

Single electron transfer, nucleophilic additions and cycloadditions are three distinct classes of important organic reactions. Can we apply our knowledge in structure-activity relationships to synthesize a molecule that can potentially undergo these three reactions? Can we set conditions to make these molecules react selectively through a particular pathway? Our attempts to answer these two questions are described in this thesis.

Thanks to their low ionization potentials, organic sulfides undergo fast one electron oxidation reactions. Suitable oxidants can remove an electron from a lone pair on sulfur to form the corresponding radical cations which can be used for probing mechanisms of electron transfer quenching of excited states as well as for monitoring the fate of the sulfur radicals.

Sulfur compounds are also good Michael donors. Michael addition reaction is a well-known example for two electron transfer reaction. It is the most efficient and facile method to generate C−C, C−N, C−S, C−O, and other C−X bonds within the organic molecule.

Cycloaddition reaction constitutes another important class of organic reactions. Diels-Alder reaction is an efficient route for the formation of carbon-carbon, carbon-heteroatom and heteroatom-heteroatom bonds in organic synthesis. Anthracene

and its derivatives undergo efficient Diels–Alder reaction with alkenes under thermal and photochemical conditions.

Organic sulfides containing anthracene components can undergo one electron transfer, two electron transfer and Diels-Alder reactions. So we have selected (anthracen-9-yl)methyl sulfides, having 'acceptor-spacer-donor' geometry as the right substrates to examine multiple reactivity. Here the spacer shuts direct electronic communication between anthracene and sulfide components enabling the units to react independently. Our aim was to examine the effects of solvent, substrate concentration and temperature on one electron transfer, two electron transfer and Diels-Alder reactions in sulfides. These acceptor-spacer-donor type anthracenemethyl sulfides are likely to undergo efficient photoinduced electron transfer reactions.

In this context, the thesis entitled "***Investigations on electron transfer reactions of a few anthracenemethyl sulfides with suitable electron acceptors and related studies*"** clearly explains the effect of nature of solvent, concentration and temperature of the reaction between a few (anthracen-9-yl)methyl sulfides with electron acceptors like DMAD, DBA and DBE. In addition, we examined photoinduced electron transfer reactions of (anthracen-9-yl)methyl sulfides and photochemical reactions of (anthracen-9-yl)methyl sulfide derived dibenzobarrelenes.

The thesis is organized into five chapters. The first chapter briefly introduces one electron transfer, two electron transfer and Diels-Alder reactions of sulfides. The outline of the research

problem is defined at the end of this chapter. The second chapter describes the synthesis of a few (anthracen-9-yl)methyl sulfides through a simplified reaction protocol developed by us. Third chapter describes the reactions of (anthracen-9-yl)methyl sulfides with suitable dienophiles in different solvents. Here we have clearly demonstrated the effects of nature of substrate and solvent, concentration and temperature on the reaction between (anthracen-9-yl)methyl sulfides and electron acceptors. Fourth chapter gives details on photoinduced electron transfer reactions of (anthracen-9-yl)methyl sulfides. Results of the photochemical transformations of (anthracen-9-yl)methyl sulfide derived dibenzobarrelenes are described in chapter five.

Each chapter of the thesis is as an independent unit and therefore the structural formulae, schemes, figures and charts are numbered chapter-wise. All new compounds are fully characterized on the basis of their spectral and analytical data. Relevant data for the characterization of novel compounds synthesized by us are reported and relevant references are cited for alternative synthesis and physical data for known compounds. A comprehensive list of references is included at the end of each chapter.

List of Abbreviations

AcOH	: acetic acid
br	: broad
CTC	: charge transfer complex
d	: doublet
DBA	: dibenzoylacetylene
DBE	: dibenzoylethylene
DCA	: dicyanoanthracene
DCM	: dichloromethane
dd	: doublet of doublet
DMAD	: dimethyl acetylenedicarboxylate
DMF	: dimethylformamide
E	: entgegen
EDA	: electron donor acceptor
ET	: electron transfer
EWGs	: electron withdrawing groups
HOMO	: highest occupied molecular orbital
ISET	: inner-sphere electron transfer
LUMO	: lowest unoccupied molecular orbital
m	: multiplet
MeOH	: methanol
g	: gram
mL	: millilitre
NMR	: nuclear magnetic resonance
OSET	: outer-sphere electron transfer
PET	: photoinduced electron transfer
quin	: quintet
R	: rectus
RT	: room temperature
s	: singlet
S	: sinister
sep	: septet
SET	: single electron transfer
S_N1	: substitution nucleophilic (unimolecular)
S_N2	: substitution nucleophilic (bimolecular)
SOMO	: singly occupied molecular orbital
$S_{RN}2$	: substitution radical nucleophile bimolecular
t	: triplet
TS	: transition state
Z	: zusammen

CONTENTS

CHAPTER 1

ELECTRON TRANSFER REACTIONS OF SULFIDES - AN OVERVIEW

1.1. Abstract

Herein we present a discussion on electron transfer processes. We have discussed both one electron and two electron transfer reactions of sulfides and Diels-Alder reactions. We have also presented a conceptual picture of photoinduced electron transfer processes given by sulfides.

1.2. Electron Transfer Reactions – A General Study

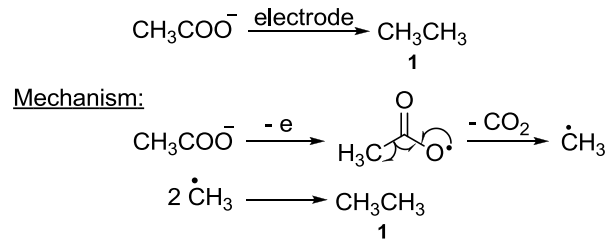
Chemical reactions involve breaking and making of bonds between atoms, chemical conversion always involves shifting of electrons between atoms. Thus, the mechanism of transfer of electrons, which leads to chemical conversions, is rather fascinating. Electron transfer reactions are among the most abundant and fundamental of all chemical processes, with wide ranging implications throughout many areas of chemistry, physics

and biology.[1,2] Nature exploits a variety of electron transfer reactions to accomplish numerous important biological processes apparently because these reactions are extremely very fast and which can take place between well separated moieties which can be induced by light and can initiate secondary reactions. These processes include respiration, photosynthesis, nitrogen fixation, neurotransmitter metabolism and the immune response. Aerobic respiration and photosynthesis harvest most of the energy required to support life and essentially maintain the global carbon, hydrogen and oxygen cycles. There are proteins that enable electron transfer from one part to another. A few of such systems are: cytochromes, ferridoxins, rubredoxins, xanthine oxidase, aldehyde oxidase, succinate dehydrogenase, stellacyanin, plastocyanin, azurin, etc.[3] These proteins contain metal ions capable of switching between different oxidation states to transport electron.

Electron transfer chemistry has been widely used in numerous ways in many areas since 1950's and the inventive research work of Rudolph A. Marcus represents basic platform for the design of electron transfer theory. Marcus theory provides a thermodynamic and kinetic framework for describing electron transfer mechanisms. Heterogeneous ET at solid electrodes is of particular scientific and technological significance. It is a subject of theoretical and methodological efforts in electrochemistry.[4,5] The classic Marcus-Hush (MH) theory for homogeneous ET kinetics in solutions was adopted to treat heterogeneous ET kinetics.[4,6-8] In comparison with the phenomenological Butler-

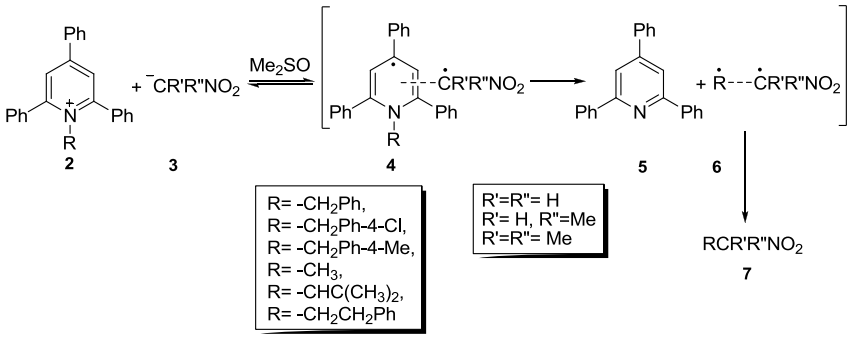
Volmer (BV) theory, the MH model provides physical insight into the activation of an ET process, namely, the reorganization of the inner ligands in the redox species together with the outer solvent shells of redox species to reach the iso-energetic electronic states at which electron tunnelling occurs according to the Franck-Condon principle.[4,5,8] Electron transfer chemistry has been widely used for the development of semiconductor devices,[9,10] polymers,[11] solar energy conversion,[12,13] chemiluminescence,[14,15] organic or inorganic synthetic methods,[16,17] site-directed mutagenesis,[18] chemically modified proteins[19] etc.

Most of the organic reactions are considered to proceed by a two-electron transfer mechanism, even though both biology and radical chemistry rely extensively on one-electron transfer processes. Radicals generated by homolytic cleavage of compounds were traditionally employed in the industrial production of polymers and for the synthesis of organic molecules.[20] In 1834 Michael Faraday reported the first preparation of organic compounds at electrodes.[21] He synthesized ethane (**1**) by using single electron transfer mechanism (Scheme 1.1).



Scheme 1.1

Since the early 20th century when electron-donor (D) and electron-acceptor (A) organic molecules are brought into contact, they form an electron donor-acceptor (EDA) complex, also known as a charge transfer complex (CTC), with partial charge transfer or one electron being transferred from the donor to the acceptor. In the reaction of *N*-(primary alkyl), *N*-(secondary alkyl) and *N*-benyl-2,4,6-triphenylpyridiniums **2** with nitronate anions **3** derived from nitromethane, nitroethane and 2-nitropropane yields the corresponding *C*-alkylated nitro compounds **7** in preparatively useful reactions.[22,23] The *N*-benzyl transference from *N*-benzyl-2,4,6-triphenylpyridiniums in Me_2SO to 2-nitro-propanide proposed a novel $S_{RN}2$ (substitution radical nucleophile bimolecular) mechanism. They termed it as a "nonchain radicaloid" mechanism which involves the intermediate formation of a CTC **4** between **2** and **3** in an equilibrium. The CTC then decomposes to give the radical of *N*-substituent **6** and pyridine (**5**). *N*-substituent radical combines with nitronate radical to give the product **7**[23] (Scheme 1.2)



Scheme 1.2

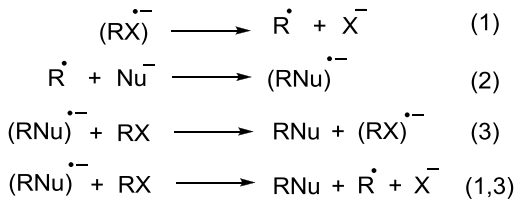
Later the theory of EDA complexes and of the SET in organic compounds was elaborated, inner-sphere electron transfer (ISET) refers to SET between two metal centers containing a bridging ligand, while outer-sphere electron transfer (OSET) refers to SET in the absence of a bridging ligand.[24-27] The distinction between OSET and ISET was defined on the basis of interactions of metal centres in the complexes. H_{DA} is the donor-acceptor interaction enthalpy. The OSET process refers to a SET process characterized by a transition state in which the donor and acceptor interact weakly (H_{DA} < 1 kcal/mol), while ISET refers to a SET process characterized by a transition state in which the donor and acceptor interact strongly (H_{DA} > 5 kcal/mol).

Nucleophilic substitution reactions are prominent with both aliphatic and aromatic substrates. In aliphatic family the nucleophilic substitution proceed through the classical polar bond forming-bond breaking S_N1, S_N2 and related mechanisms involving transfer of a pair of electrons. In the aromatic family, two electron processes such as S_NAr, benzyne and halogen-metal exchange mechanisms usually account for nucleophilic substitution reaction. The addition reactions of unsaturated aliphatic compounds are two electron transfer process. Mechanism of nucleophilic substitution varies greatly with the nature of the substrate, the nucleophile and the reaction conditions.[28]

Besides this relatively wide polar mechanistic spectrum, many systems react very slowly or remain unreactive through any of these substitution mechanisms. Their less reactivity is usually

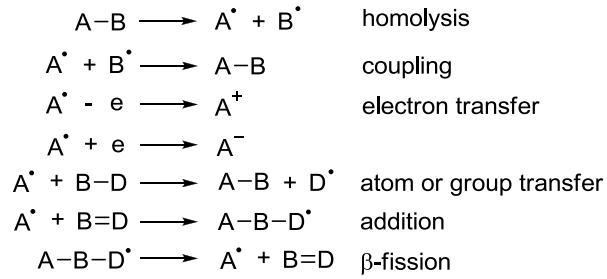
due to strain (cycloalkyl and polycycloalkyl halides), steric (cycloalkyl, polycycloalkyl, and neopentyl halides), electronic factors (unactivated aromatic and heteroaromatic substrates, vinyl halides, and perfluoroalkyl halides) or a combination of them.[29] For such compounds the nucleophilic substitution can be accomplished by mechanisms that involve electron transfer steps. There are compounds in which both polar and electron transfer routes are feasible. An example is alkyl halides substituted by π acceptor EWGs. For performing ET mediated nucleophilic substitution reactions, initial radical formation in needed. The widely used methods for radical formation are chemical initiation by alkali metals in liquid ammonia,[30] electrochemical initiation at the cathode,[31] thermal ET from an adequate donor,[32] usually a charged nucleophile, and photoinitiated ET[33] from the nucleophile.[34] The latter two types of initiations are favoured between nucleophiles that are very good electron donors and substrates that are very good electron acceptors.

$S_{RN}1$ follows a chain mechanism where overall reactivity depends on the initiation, propagation, and termination steps.[35] Scheme 1.3 represents the propagation steps of the $S_{RN}1$ mechanism. In order for this process to work efficiently, the initiation step may be slow. However, the chain propagation needs to be fast and efficient in order to allow long chains to build up. Finally, the wide variety of nucleophiles can be used so that many C-C and C-heteroatom bonds can be obtained.[36]



Scheme 1.3

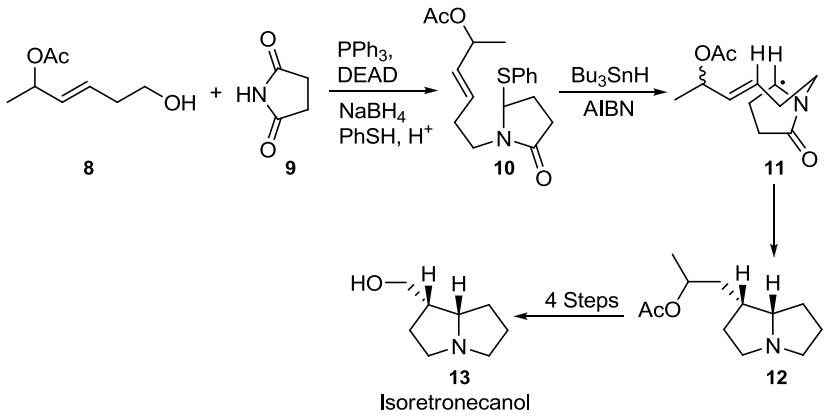
Radicals and radical ions generated from the SET processes react in coupling, single electron transfer, atom or group transfer, addition, and elimination reactions. The elementary mechanistic steps are shown in Scheme 1.4 in which A, B, and D represents atoms or groups, not necessarily carbon-centred. The atom-transfer (AT) reaction refers to the abstraction of an atom or group (GT) from an organic molecule to produce a new radical located at the former site of the abstracted functionality. The direction of the reaction is determined by its exothermic character and by the reactivity of the newly formed radical.[37] The groups commonly abstracted are hydrogen atoms, halogen atoms, as well as groups such as SR and SeR.[38]



Scheme 1.4

Tributyltin hydride is the most commonly used reagent to conduct free-radical reactions. For the synthesis of natural

products having six membered ring, the tin hydride method was first applied. The tributyltin hydride method has been extensively used for the formation of nitrogen containing heterocycles (Scheme 1.5).[39,40]



Scheme 1.5

1.3. Electron Transfer Reactions of Sulfides.

Organic sulfides are abundant in nature. These compounds are useful synthetic intermediates in many aspects of organic and medicinal chemistry with applications in bio-organic,[41,42] inorganic,[43-45] medicinal,[46-49] heterocyclic synthesis[50-52] and as key intermediates for the synthesis of biologically active compounds. Oxidation of the sulfide side chain of methionine residues in peptides and proteins has been suspected in oxidative stress and aging. These oxidations have also been a source of great interest in searches for the chemical basis of specific disease states, such as Alzheimer's disease, Jacob-Creutzfeld's syndrome, and Parkinson's disease.[53-57] Organic sulfides undergo fast one electron

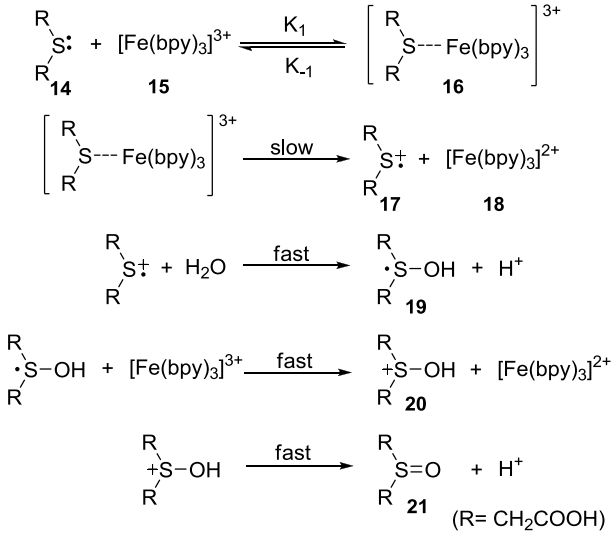
oxidation reactions, because of their low ionization potentials. Thus, suitable oxidants can remove an electron from a lone pair on sulfur to form the corresponding radical cations. It is reported that organic sulfides are ideal precursors for sulfur-centred radical cations that can be used for probing mechanisms of electron transfer quenching of excited states as well as for monitoring the fate of the sulfur radicals.[58-66]

Sulfur centred radical cations and radical cation complexes are important intermediates in a variety of chemical processes extending from those of industrial importance to biological systems. [67-74] Formation of sulfide radical cation as intermediate has been proposed in electrochemical oxidation,[75-79] in chemical oxidation with Fe(III),[80] Ce(IV),[81] Cr(VI),[82,83] Cr(V),[84,85] Mn(III),[86] Ru(IV),[87] cytochrome P-450,[88-91] peroxidase,[92,93] in photosensitized oxidation[94-104] and in the irradiation of the charge-transfer complex of sulfides with electron acceptors.[105-107]

1.3.1. Sulfide Oxidation by Suitable Chemical Oxidants.

A variety of chemical oxidants initiate electron transfer reactions of sulfides.[80-93] Biologically important organic sulfides undergo electron transfer reactions with several metal ions to generate sulfide radical cations that are of great concern in biochemical processes. Iron(III)-polypyridyl complexes undergo efficient electron transfer reaction with aryl methyl and dialkyl sulfides, aryl methyl sulfoxides, aryl thioacetic acid and sulfur

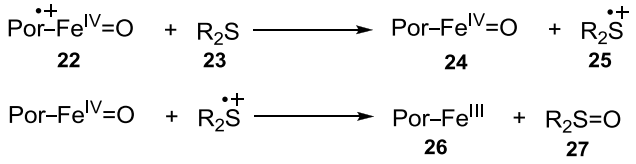
containing amino acids. Results from kinetic and product analysis studies indicate that iron(III)-bipyridyl complex is capable of transforming thiodiglycolic acid (TDGA) (**14**) to their sulfoxide **21** via single electron transfer mechanism.[108] Mechanism for the electron transfer reaction of tris(2,2'-bipyridine) iron(III) complex (**15**) with TDGA is shown in scheme 1.6.



Scheme 1.6

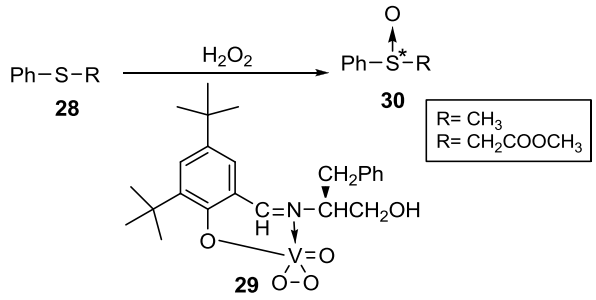
Horseradish peroxidase (HRP) is a hemoprotein peroxidase which catalyses the oxidation of sulfides to sulfoxides involving the ferryl oxygen transfer to the S atom. The reaction mechanism involves sequential electron abstraction from two substrate molecules, whereby the ferryl porphyrin radical cation ($Por^{\bullet+}$-Fe^{IV}=O), formed by reaction of H_2O_2 with the ferric enzyme, is reduced first to Por-Fe^{IV}=O, and then to the resting ferric state **26**.[109-112] Here the electron transfer from the sulfide **23** to ($Por^{\bullet+}$-

Fe^{IV}=O) takes place to give the radical cation $R_2S^{\bullet+}$ which then reacts with Por-Fe^{IV}=O to form sulfoxides **27**, the oxygen rebound step (Scheme 1.7).



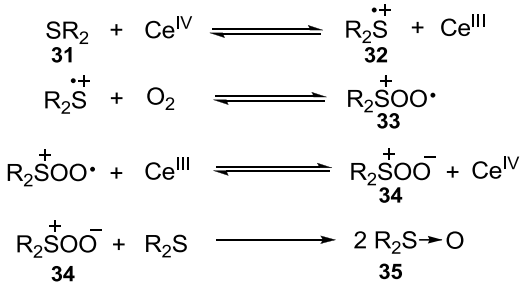
Scheme 1.7

Asymmetric oxidation of sulfides by hydrogen peroxide in the presence of vanadium (IV) complexes with chiral Schiff bases is an exceptionally simple experimental procedure for the preparation of chiral sulfoxides.[113] Single-step addition of all the necessary amount of hydrogen peroxide results in increase in the temperature of the reaction medium which leads to the formation of sulfones and hence hydrogen peroxide is added dropwise, at a non-specified rate though, to avoid this undesirable temperature effect. Probably, asymmetric oxidation of thioanisol and methyl phenylthioacetate is catalysed by chiral vanadium monoperoxo complexes **29** to yield chiral sulfoxides **30** (Scheme 1.8).



Scheme 1.8

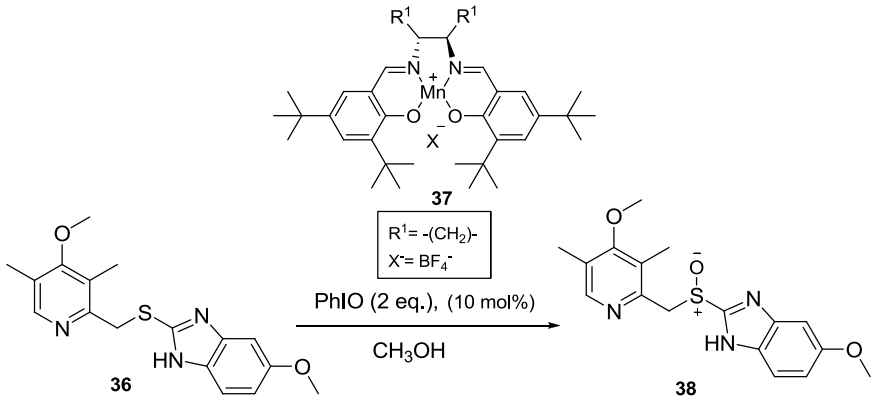
Organic sulfides can be oxidized with catalytic amounts of Ce^{IV} salts rapidly and selectively to sulfoxides using molecular oxygen (P_{O_2}= 5-15 bar) as the oxidant. Addition of a catalytic amount of Ce^{IV} salt accelerates the autoxidation of organic sulfides **31** by at least a factor of 10^3, even at lower pressures and temperatures, affording a synthetically useful reaction. Ce^{IV} satisfies the thermodynamic requirements for oxidation of a sulfide, thus facilitating electron transfer to yield the sulfur radical cation **32**. Oxygenation of **32** gives oxygenated radical cation **33** which in turn oxidizes Ce^{III} back to Ce^{IV} with production of the zwitterion **34**. This reaction may also proceed as a chain reaction in which the role of Ce^{IV} is as an initiator only. Zwitterionic species **34** reacts with an additional sulfide to yield sulfoxides **35** (Scheme 1.9).[114]



Scheme 1.9

Choi *et al.* have developed an efficient asymmetric oxidation of sulfides using chiral Salen-Mn(III) catalysts under mild conditions. These sulfoxides act as important chiral auxiliaries in a variety of highly diastereoselective carbon-carbon

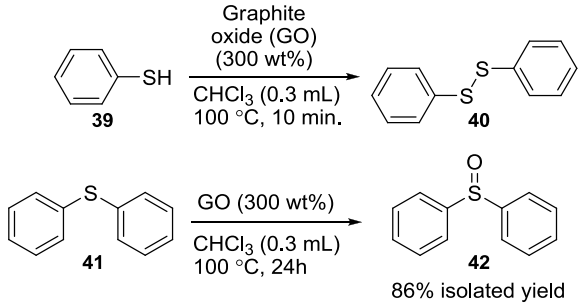
bond forming reactions, including the synthesis of chiral amines, amino acids, aziridines, and amino phosphoric acids.[115] Moreover, enantiomerically pure sulfoxides are widely used as drug intermediates, such as esomeprazole and eslansoprazole and modafinil. The catalyst Salen-Mn(III) complex **37**, activated by a tetrafluoroborate anion, was used and the reaction takes place slowly with the formation of esomeprazole (**38**) in 58% yield with 69% ee in the presence of iodosylbenzene as the oxidant[116] (Scheme 1.10).



Scheme 1.10

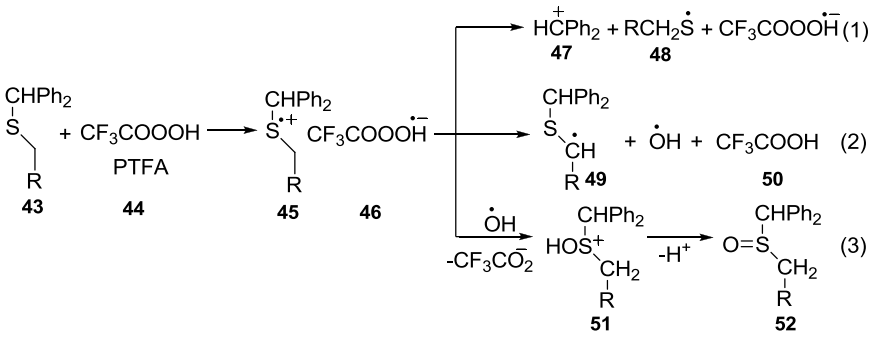
Graphite oxide (GO), a heterogeneous carbocatalyst obtained from low cost, commercial starting materials effectively facilitates oxidation of thiols **39** and sulfides **41** to their corresponding disulfides **40** and sulfoxides **42**, respectively, and with good selectivity. These reactions require relatively short reaction time (as brief as 10 min) and which has high product recovery yield, since the purification of product was facilitated by

GO's heterogeneous nature and disappearance of over-oxidation of sulfur compounds (Scheme 1.11).[117]



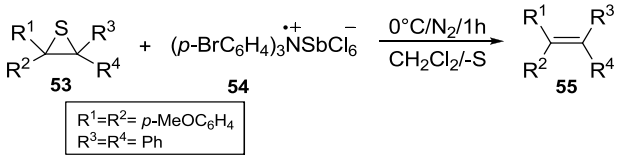
Scheme 1.11

Peroxytrifluoroacetic acid (PTFA) readily oxidizes thiophenes and dibenzothiophene to sulfoxides or even to sulfones[118,119] whereas some alkanes and cycloalkanes are oxidized to alcohols. These properties of peroxy acids and relatively low ionization potentials and standard redox potentials of sulfides should, evidently, favor sulfoxidation via an alternative single electron transfer mechanism. Reactions of benzhydryl sulfides Ph_2CHSCH_2R (R = H, $CONH_2$, COOH, CN) with peroxytrifluoroacetic acid in CF_3COOH were studied experimentally. Electron transfer from benzhydryl sulfides **43** to PTFA **44** can be accompanied by three types of secondary processes involving the radical cations **45**: (1) detachment of the benzhydryl carbocation from these radical species; (2) their α-deprotonation (for instance, by the action of the PTFA radical anion), resulting in the products of C-H fragmentations; and (3) recombination with the hydroxyl radical (with the formation of *O*-protonated sulfoxides) (Scheme 1.12).[120]



Scheme 1.12

An efficient preparation of arylsubstituted olefins from corresponding thiiranes in high yields under mild conditions has been reported. Here tris-(*p*-bromophenyl)aminium hexachloroantimonate (**54**) is used as the single electron transfer oxidant. The reaction is initiated by SET from thiiranes **53** to aminium radical salt to form the thiirane radical cation and tris-(*p*-bromophenyl)amine. C-S bond cleavage followed by desulfurization leads to the radical cation. SET from tris-(*p*-bromophenyl)amine to the radical cation generates the corresponding olefin **55** (Scheme 1.13).[121]



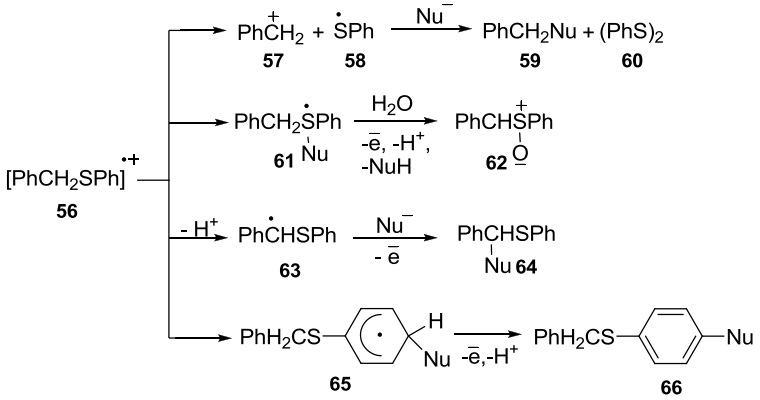
Scheme 1.13

1.3.2. Electrochemical Studies on Sulfides.

Electrochemical studies of aromatic and aliphatic sulfides have received considerable attention from time to time. Both reduction and oxidation processes of these compounds have been well studied by electrochemical methods. Electrochemical oxidation of sulfide provides sufficient oxidative cleavage of C-S bonds for generating various carbocation intermediates which form new C-C or C-hetero atom bonds by the attack of nucleophiles.[122,123] Sulfide oxidation is difficult without affecting the nucleophiles because the oxidation potentials of nucleophiles are often lower than those of sulfides, and also the oxidation potentials of products are comparable to those of the starting materials.

Electrochemical oxidation of alkyl phenyl sulfides (PhSR) has been studied extensively by Torii, S. *et al.*[124,125] Both polarography and cyclic voltammetry results suggest that the primary oxidation step of the phenyl sulfides involves one electron transfer. Anodic oxidation of phenyl sulfides initially takes place at phenylthio group to provide sulfide radical cation which readily undergoes chemical or electrochemical reactions depending on the structures of phenyl sulfides. Products of these reactions are remarkably dependent upon the structure of R, polarity of the solvent, and the supporting electrolyte.[126] If R can yield stabilized carbocations like benzyl or triphenylmethyl cations, extensive cleavage of the C-S bond occurs during oxidation (Scheme 1.14).

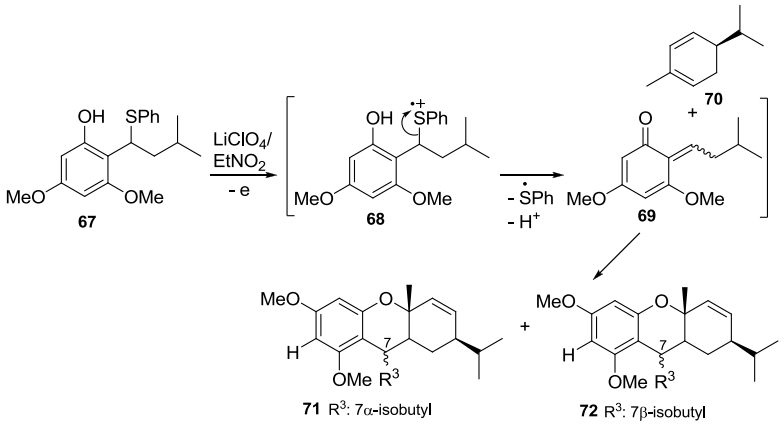
With other R groups the corresponding sulfoxides or sulfones are obtained in good yields, especially when the electrolyses are performed in solvents containing water.[127,128] Alternative reaction pathways[129] consist of C_α-H deprotonation of the sulfide radical cation or substitution of the phenyl ring at the *p*-position. The former reaction is strongly favoured in acetic acid as a solvent and is more likely to occur in the case of the less bulky alkyl groups, while the latter reaction can be suppressed by using *p*-substituted aryl thioether.[130] Alternative electrooxidation pathways of benzyl phenyl sulfides is shown in scheme 1.14.



Scheme 1.14

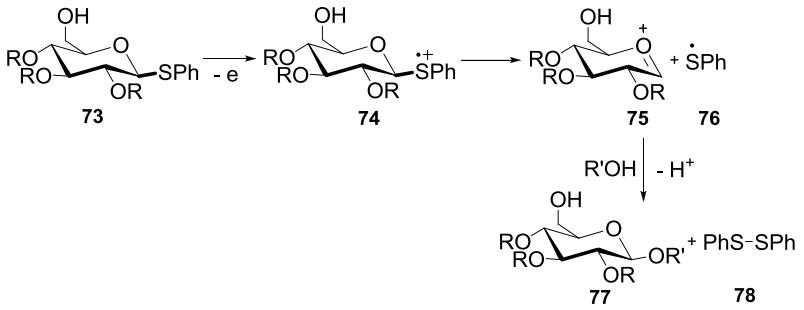
Electrochemical oxidation of *o*-[1-(phenylthio)alkyl]phenols **67** in lithium perchlorate-nitroalkane gives corresponding *o*-quinone methides **69**, which are trapped by unactivated alkenes **70** to form chromanes including euglobal skeletons **71** and **72**.[131] Lithium perchlorate-nitromethane system was found to accelerate Diels-Alder reaction of quinones generated

in situ by electrochemical oxidation.[132] Scheme 1.15 shows the proposed reaction of robustadials and euglobals.



Scheme 1.15

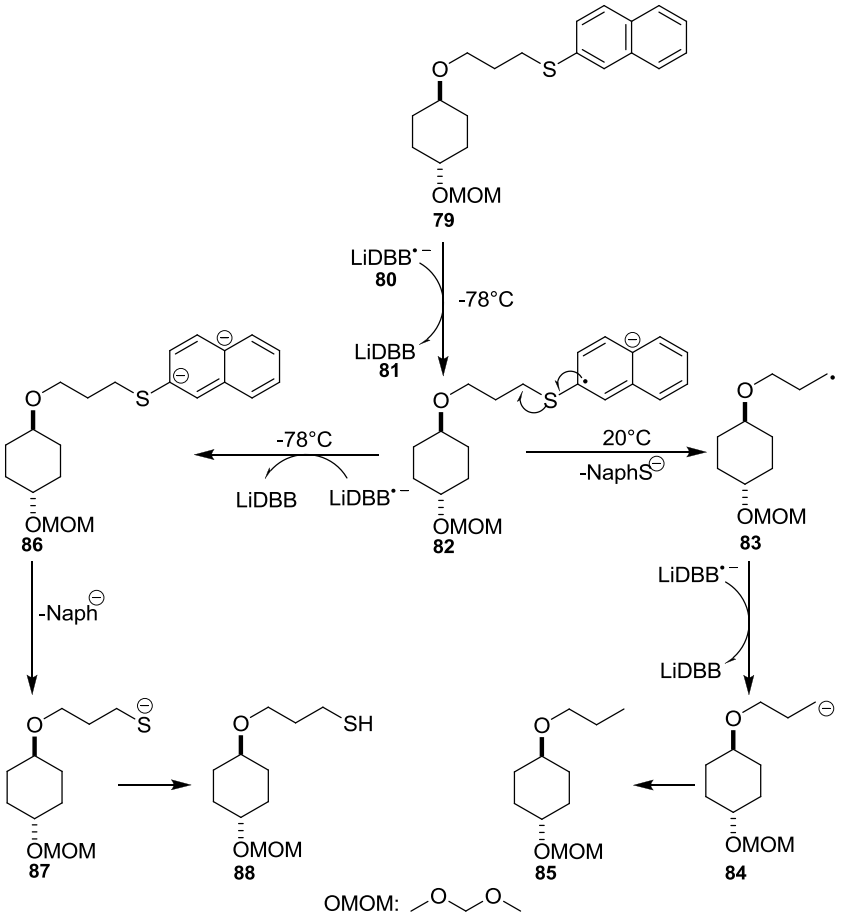
Unprotected aryl thioglycosides undergo an efficient electrochemical oxidation in undivided cell at constant moderated potential in the presence of alcohols to give the corresponding glycosides in good yield without the formation of any self-condensation products. Phenyl thioglycosides **73** undergo anodic oxidation to form sulfide radical cation and then C-S bond cleavage takes place to form the classical stabilized oxocarbenium ion **75** which is considered as intermediate in numerous glycosylation reactions.[133] The reaction occurred at a lower oxidation potential allowing the use of a large variety of functional groups in the nucleophilic partner (Scheme 1.16).



Scheme 1.16

Single electron transfer mediated reductive cleavage of functional groups has been widely utilized in synthetic organic chemistry. As part of a synthetic study, 2-[(3-{[*trans*-4-(methoxymethoxy)cyclohexyl]oxy}propyl)thio]naphthalene **79** was treated with 4,4'-di-*tert*-butylbiphenyl and lithium metal **80** at different temperatures, 20 ºC, 0 ºC and -78 ºC in tetrahydrofuran (THF) that show a change in the cleavage mechanism based solely upon temperature control of the SET reaction. The mechanism of reductive cleavage was proved by a detailed electrochemical analysis using platinum electrodes in THF and controlled-potential bulk-electrolyses at 20 ºC and -78 ºC.[134] Following a series of SET reductions performed on the naphthyl thioether **79**, the cyclic voltammetry technique is used to determine the mechanism of reductive cleavage. At 20 ºC, the thioether accepts a single electron before dissociating at the alkyl carbon–sulfur bond. At -78 ºC, the thioether is stabilized at sufficiently longer time scales to accept two electrons in a stepwise fashion. The dianion **86** then cleaves selectively at the aryl-sulfur bond, forming the alkyl thiol **88**. Scheme 1.17 shows the cleavage pathways following reduction

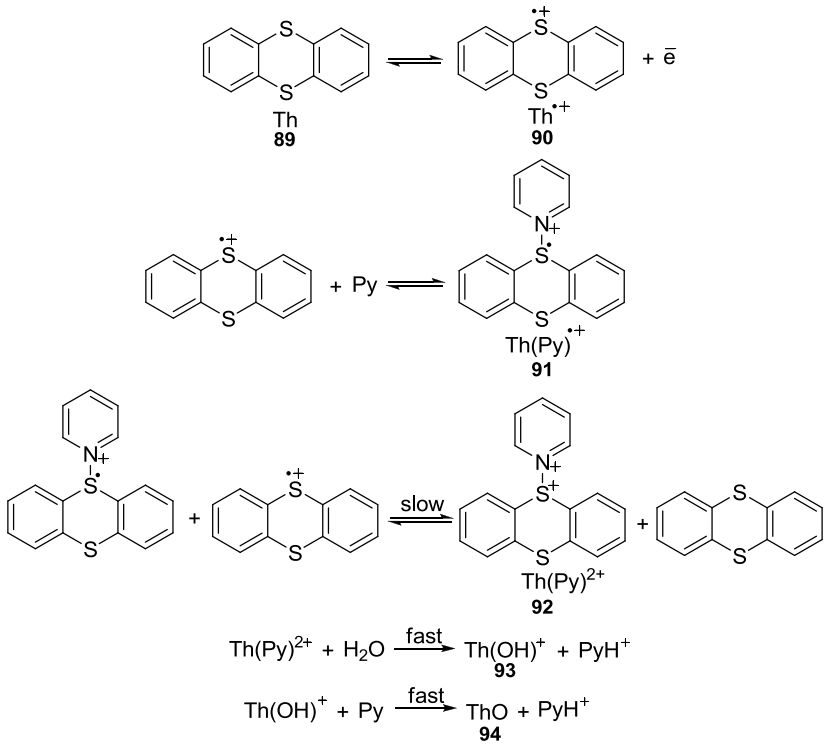
of thioether under single electron-transfer conditions at 20 ºC and -78 ºC. Using the cryoelectrochemical procedure, electrochemical parameters such as the half wave potential, $E_{1/2}$, peak potential, E_P etc. can be determined accurately.



Scheme 1.17

The role of cation radical/nucleophile adduct deprotonation equilibria in the reactions of thianthrene cation radical **90** with pyridine and water in acetonitrile solution has been examined using stopped-flow and electrochemical techniques. The protic and

aprotic nucleophile such as water and pyridine, upon their respective reactions with the cation radical of thianthrene suggests a half-regeneration mechanism.[135] In both reactions reversible nucleophilic attack and adduct formation at a sulfur site on **90** is proposed as the first step in a general half-regeneration scheme. Cyclic voltammetric behaviour of **89** at a platinum electrode in anhydrous acetonitrile reveals that the oxidative process observed at a potential of +1.25 V which is attributed to the oxidation of **89** to **90**. The rate-determining step involves electron transfer from a pyridine/cation radical sulfur bonded adduct **91** to a nonadducted cation radical (Scheme 1.18).[136] The product of this step [the N-S dication, **92**] is extremely reactive and it undergoes rapid hydrolysis to form the protonated oxide [$Th(OH)^+$, **93**] and PyH^+. Subsequent fast deprotonation by a second Py molecule yields the final addition product, ThO, **94**.

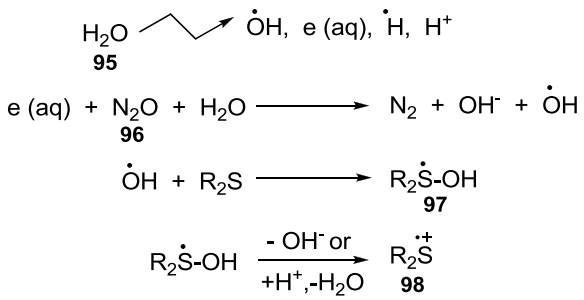


Scheme 1.18

1.3.3. Radiation Chemical Studies of Sulfides

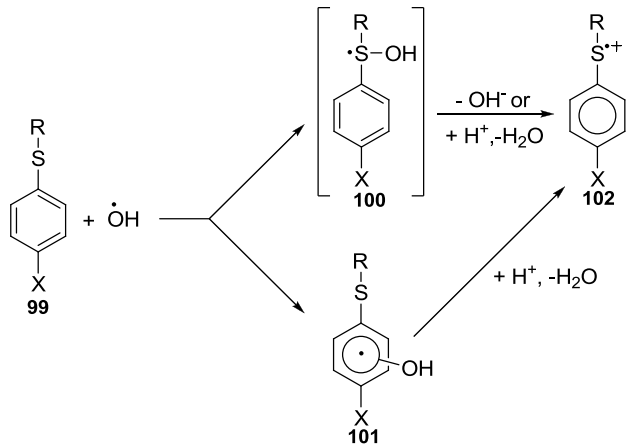
Radiation chemical studies are among the most convenient methods for the analysis of the reactivity and properties of sulfide radical cations. Radiation induced chemical reactions take place in nanosecond and in microsecond time scale and can be easily monitored by spectrophotometric and conductimetric detection techniques.[137-139] Sulfide radical cations can be generated by reaction of sulfides with hydroxyl radicals ($OH^{\bullet}$) generated by radiolysis of water (Scheme 1.19). Solvated electrons are also

produced, which can be rapidly and efficiently scavenged by N_2O to produce more $OH^{\bullet}$.[140-143]



Scheme 1.19

Oxidation mechanisms involve addition of $OH^{\bullet}$ to S atom with the formation of hydroxysulfuranyl radical intermediates. These reactive species can be stabilized by the presence of electron-withdrawing substituents.[144] One-electron oxidation by hydroxyl radicals adsorbed on the TiO_2 surface produced after pulse radiolysis in colloidal TiO_2 aqueous solutions has also been reported for the production of 4-methylthiophenylmethanol and 2-phenylthioethanol radical cations.[145] In the reaction of aromatic sulfides with $OH^{\bullet}$ [146-149] produced by radiolysis of water, there exists two competitive pathways depending upon the nature of substituents present in the molecule. The two pathways are (i) addition of $OH^{\bullet}$ to the thioether functionality leading to a monomeric sulfur radical cation and (ii) addition to the aromatic ring leading to hydroxycyclohexadienyl radicals followed by H-abstraction leading to α-thio radicals (Scheme 1.20).

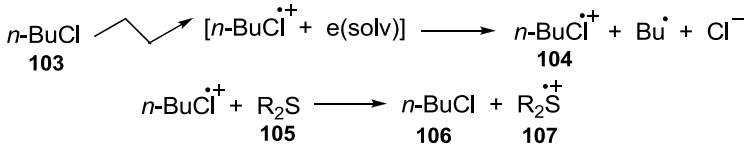


Scheme 1.20

Sulfide radical cations can be generated by oxidation with specific one-electron oxidants such as $SO_4^{\bullet-}$, Tl^{2+} and $Br_2^{\bullet-}$, $Cl_2^{\bullet-}$, $N_3^{\bullet}$ and $CCl_3OO^{\bullet}$ generated from the primary reactive species formed after water radiolysis.[150-155] Influence of hydroxypropyl-β-cyclodextrin on one-electron oxidation reaction of aromatic sulfides with $Br_2^{\bullet-}$ and the decay process of the aromatic sulfide radical cation was investigated by pulse radiolysis. Binding ability of sulfide radical cation with hydroxypropyl-β-cyclodextrin is much lower than that of aromatic sulfide because of the hydrophobic nature of the cavity. The formation process of dimeric radical cation, which is generated between sulfide radical cation and neutral sulfide in solution, was also inhibited by the addition of cyclodextrin.[156]

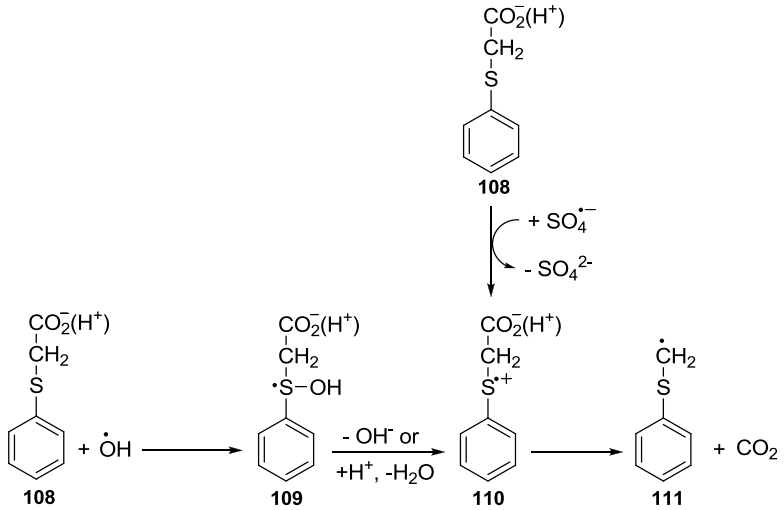
Sulfur radical cations have also been generated in non-polar media by pulse radiolysis in *n*-butyl chloride (Scheme 1.21).

Nonpolar nature of the environment diminishes the stabilization of ions by solvation.[157]



Scheme 1.21

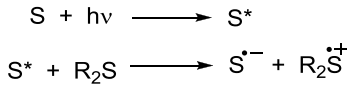
Sulfur radical cations undergo β-bond fragmentation which involves a decarboxylation process as observed in radical cations of phenylthioacetic acids.[158] The $OH^{\bullet}$, produced by pulse radiolysis in aqueous solution at low p*H* oxidises phenylthioacetic acid (**108**), led to the formation of short-lived monomeric radical cation $PhS^{\bullet+}CH_2COOH$ (**110**) and which was decayed by decarboxylation to give the radical $PhSCH_2^{\bullet}$.[147,137] Decarboxylation of phenylthioacetic acid was also observed after oxidation of the same substrate by $SO_4^{\bullet-}$ produced by pulse radiolysis of aqueous solutions containing $S_2O_8^{2-}$ and *tert*-butyl alcohol (Scheme 1.22). Decarboxylation process was confirmed by the formation of CO_2 during the γ-radiolysis of phenylthioacetic acid.



Scheme 1.22

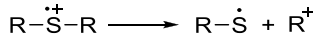
1. 4. Photochemical Reactions of Sulfides and its Synthetic Applications

Photoinduced electron transfer (PET) reactions have made exciting progress in various emerging fields during the past few decades and still continues to be in focus of numerous theoretical and experimental investigations.[159,160] Sulfides and its derivatives undergo photoinduced electron transfer reaction to form reactive sulfide radical cations. Photosensitized generation of sulfur radical cations is shown in scheme 1.23. Due to relatively low oxidation potential of organic sulfides, practically all categories of PET sensitizers can be used, such as aromatics having strongly electron withdrawing substituents[161-165], aromatic ketones,[166-168] quinones,[169-171] electron-poor heterocycles and salts[172-174] and titanium dioxide.[175-179]



Scheme 1.23

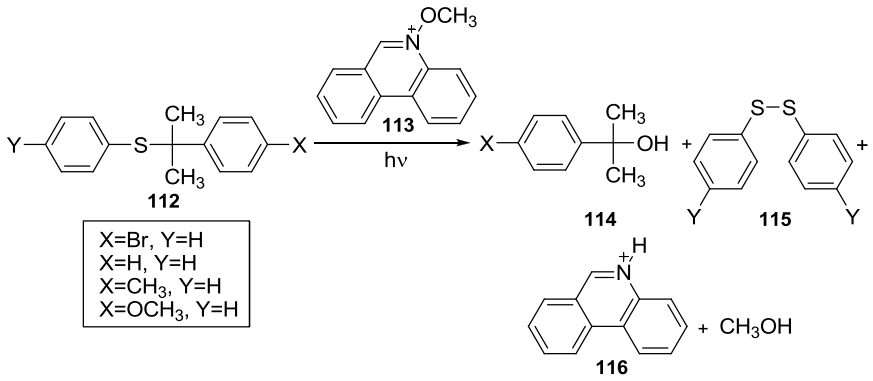
Sulfide radical cations undergo a variety of transformations and are characterized by a reactivity pattern that is very different from that of the corresponding neutral precursors.[180] Processes that are not possible with the neutral sulfides are possible with the corresponding radical cations. Different reactivity patterns of sulfide radical cation include electron transfer processes, addition of nucleophiles, reactions with O_2, S-abstraction and fragmentation reactions. Among the reactions of sulfur radical cations, C-S fragmentation occurs to form an alkyl cation and a sulfenyl radical (Scheme 1.24). When the SOMO is mostly located on sulfur, the cleaved C-S bond is α to the SOMO on the sulfur atom (α-fragmentation).[181]



Scheme 1.24

A steady state and laser photolysis study of the C-S bond cleavage of radical cations of a series of substituted aryl cumyl sulfides revealed that the fragmentation rate depends only to a very limited extent on the strength of the C-S bond in the radical cation and that the reorganization energy of the process is influenced by the structure of the alkyl groups. Also steric effects might play a significant role on the rate of the fragmentation process. DFT

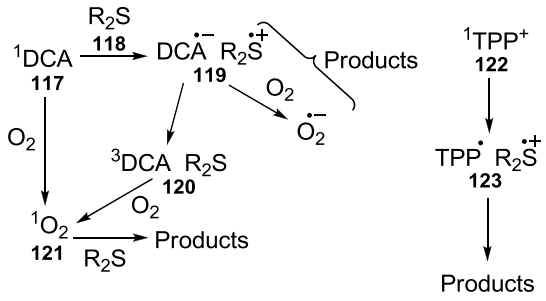
calculations have been also carried out for radical cations in order to garner information on the geometry of the radical cations and more importantly on their charge and spin distribution. This information was necessary for understanding the dynamics of fragmentation process and also a deep insight on the SOMO location. Steady state photolysis experiments were carried out for the photochemical generation of sulfide radical cations by *N*-methoxyphenanthridinium ion (**113**).[181] Photolysis of sulfides **112** generates fragmentation products in substantial amounts (Scheme 1.25). Substituted diphenyl disulfide **115** from the sulfide moiety and 2-aryl-2-propanols **114** from the cumyl group were obtained. Other products observed were those deriving from the N-O fragmentation of the phenanthridinium ion (protonated phenanthridine and methanol).



Scheme 1.25

PET is a method that can be classed among the 'extreme energy' methods, since it is based on high-energy intermediates

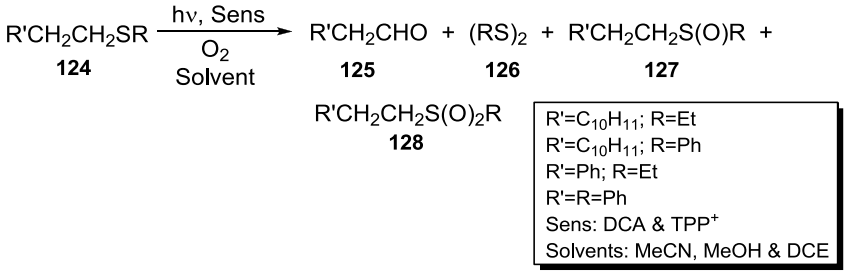
such as radical ions and is characterized by very mild, environmental-friendly conditions. Photosensitized oxidation of sulfides may involve activation of oxygen, of the sulfide or of both species. Two sensitizers, 9,10-dicyanoanthracene (DCA) and 2,4,6-triphenylpyrylium (TPP^+) tetrafluoroborate are able to oxidize sulfides. In PET-induced process these two sensitizers differ in two aspects: (i) in the former case, a radical ion pair **119**; and in the latter, a radical/radical ion pair **123** is formed; and (ii) their behaviour with oxygen. Singlet excited DCA accepts an electron from the sulfide **118** and combines with the sulfide radical cation to form the radical ion pair **119**. It undergoes secondary electron transfer to give superoxide.[182-184] The radical ion pair may, however, also undergo intersystem crossing to ^{3}DCA, and this gives singlet oxygen, possibly arising also via direct quenching of ^{1}DCA.[182,183] On the contrary, $^1TPP^+$ is known as an inefficient oxygen sensitizer and $TPP^{\bullet}$ is not sufficiently reducing to give superoxide (Scheme 1.26).



Scheme 1.26

For PET ractions of sulfides with DCA and TPP^+, competition between different paths are also affected both by

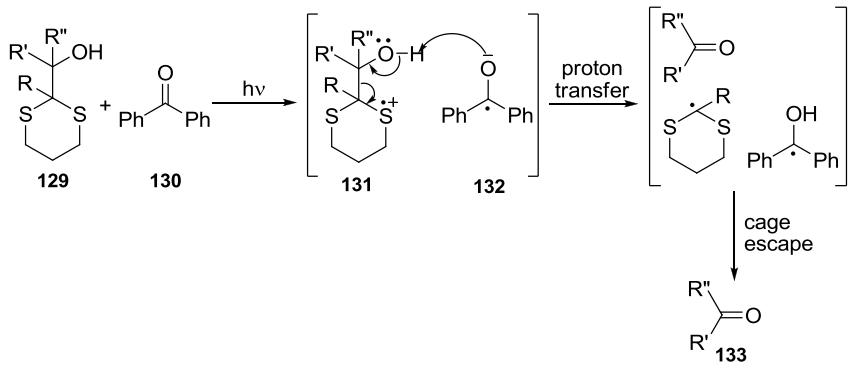
structure of sulfides and nature of medium. Oxidation rate is higher for DCA, with TPP^+ it is less efficient. Two processes are observed: sulfoxidation and oxidative cleavage of the C–S bond. With aliphatic sulfides using DCA as the sensitizer the sulfoxidation path is the major one where as with phenyl sulfides, the sulfoxide formation is a minor pathway and it undergoes reaction via C-S bond cleavage to form aldehydes (Scheme 1.27).[185] The reaction gives a mixture of products and it seems better suited for the elimination of undesired sulfur-containing pollutants, e.g. from fossil fuels,[186,187] from exhaust of meat rendering plants,[188] and from industrial waste water[189] rather than for preparative purposes.



Scheme 1.27

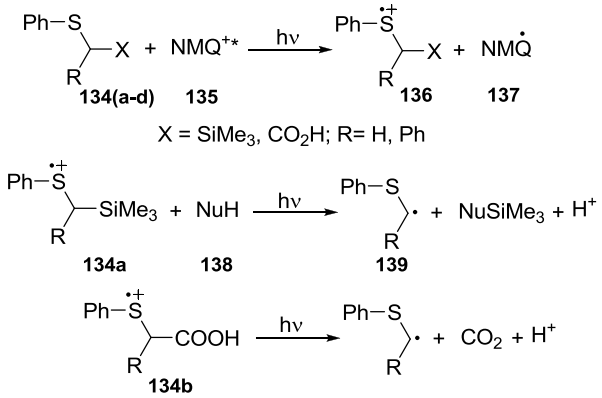
Peter Vath and coworkers reported that in dithianes the C-C bonds are weakened by photoinduced electron transfer and the cleavage occurs efficiently and selectively. This photochemical reaction is used for uncaging protected aldehydes and ketones. The mechanism involves (i) photoinduced electron transfer from the dithiane moiety to an excited benzophenone and (ii) benzophenone

radical anion assisted *O*-deprotonation coupled with C-C bond scission. The results of laser flash photolysis studies on photosensitized C-C bond cleavage of dithiane-carbonyl adduct[190] are consistent with the proposed electron transfer mechanism (Scheme 1.28).



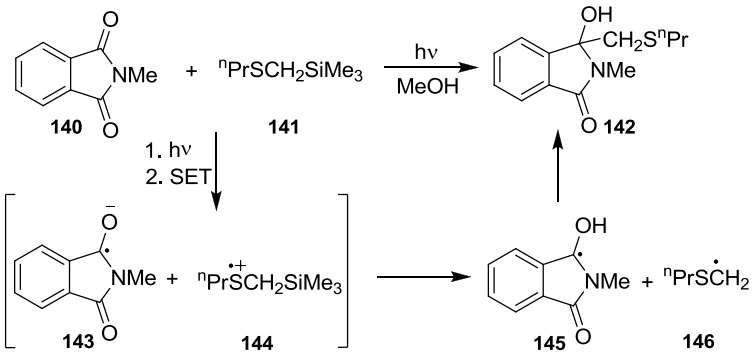
Scheme 1.28

Laser and steady-state photolysis in acetonitrile of the silyl sulfides and the phenylthioacetic acids with *N*-methylquinolinium tetrafluoroborate (NMQ^+) as the sensitizer, lead to the corresponding radical cations.[191] These radical cations undergo a fragmentation reaction which involves C-Si bond cleavage in silyl sulfide radical cation and C-C bond cleavage, with CO_2 loss in phenylthioacetic acids (Scheme 1.29).



Scheme 1.29

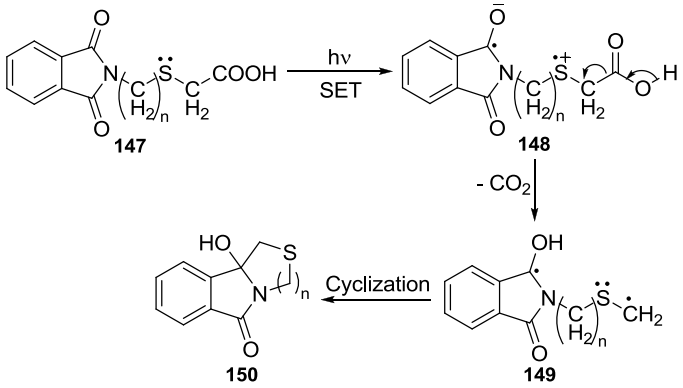
SET-induced excited state reactions of phthalimides with α-trialkylsilyl substituted thioethers proceed through pathways involving the generation and desilylation of α-silicon substituted cation radical intermediates (Scheme 1.30). In phthalimide SET-photochemistry, thioethers **141** undergo efficient photoadditions to phthalimide and its *N*-methyl derivative **140** to form the adduct **142**.[192,193]



Scheme 1.30

Upon irradiation, (ω-phthalimidoalkylthio)acetic acids undergo photocyclization in methanol with high degree of

chemoselectivity and regioselectivity to generate heterocycles with nitrogen and sulfur in the newly formed ring of various size in which the phthalimide carbonyl carbon is bonded to the α-sulfur atom in place of the carboxyl group. These photocyclized products experience water elimination to yield olefinic products in secondary ground state reactions. Intramolecular SET in singlet excited phthalimides **147** results in the generation of zwitterionic radical intermediates which undergo selective deprotonation and decarboxylation reaction leading to biradicals **149**. These biradicals undergo cyclization to produce cyclized products **150**[194] (Scheme 1.31).



Scheme 1.31

1.5. Michael Addition Reactions

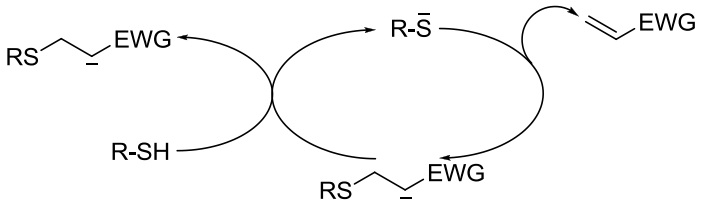
Arthur Michael discovered Michael addition reaction. It involves the addition of an enolate of a ketone or aldehyde to an α,β-unsaturated carbonyl compound at the β- carbon.[195] It is the 1,4-addition of a doubly stabilized carbon nucleophile (Michael

donor) to an α,β-unsaturated carbonyl compound (Michael acceptor) to yield highly selective products in an efficient manner under environmentally friendly reaction conditions.[196]

Michael addition reaction is thermodynamically controlled. The reaction occurs rapidly at low temperatures, offers low cure time and involves less toxic precursors.[197] It is the most efficient and facile method to generate C−C, C−N, C−S, C−O, and other C−X bonds within the organic molecule. Usually, these conjugate additions are carried out in an organic solvent in the presence of a catalyst, strong base[198] or acid.[199] But there are many serious environmental problems by using harsh catalysts and strong Lewis acids[200,201] such as $AlCl_3$, $TiCl_4$ or $SnCl_4$ which causes strongly acidic waste streams.[205] In recent times, many green routes[202-204] are available involving microwave irradiation and sonication with or without catalyst known as non-classical methods of Michael reaction. The rate of Michael addition reaction depends on the nature of solvent, substrate and base employed.[206-211] Hetero-Michael reactions such as the aza-Michael,[212-214] sulfa-Michael,[215-217] phospha-Michael[218,219] and oxa-Michael[215-217] reactions have received considerable attention in the field of organic synthesis.

The thia-Michael conjugate addition is an important process in organic chemistry and has versatile applications in biosynthesis[220] and in the construction of bioactive compounds.[221-223] In thia-Michael conjugate addition, the free thiol group in basic media are the Michael donors. The selective protection of C=C bonds of conjugated enones, can be done by thia-Michael addition

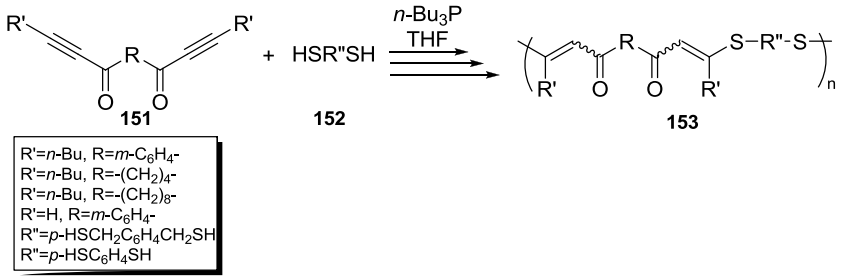
reaction and the regeneration of the double bond can be achieved by the removal of the sulfur moiety.[222,224] In the traditional base-catalyzed thia-Michael addition reaction, the reaction kinetics and yield of the thioether product obtained depends on factors such as the strength and concentration of the base catalyst, the thiol p*Ka*, the steric accessibility of the thiol and the nature of the electron withdrawing group coupled to the C=C bond. In solution reactions, the polarity of the solvent and p*H* of the solvent further affect the kinetics of the reaction.[225] Base-catalyzed thia-Michael addition reaction pathway shows the hydrothiolation of an activated C=C bond via the addition of the anion across the electron-deficient β-carbon of the ene.



Scheme 1.32

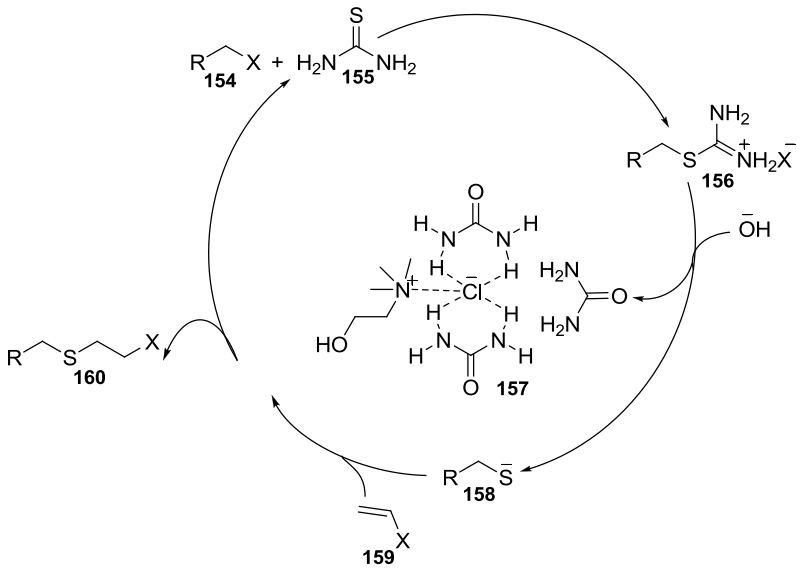
The thiol-acrylate reaction is one of the most commonly used thiol-Michael reactions and has wide applications in dendrimer synthesis, degradable hydrogel formation, surface and particle modification, and block copolymer synthesis.[226-229] Tri-*n*-butylphosphine-catalysed polyaddition of aromatic bis(ynone) having benzene ring as a spacer or aliphatic bis(ynone)s having octamethylene group and tetramethylene group as spacer with dithiols were obtained in high yield. Polyaddition of the aromatic

bis(ynone) gave a polymer composed of specifically *E*-unit, while that of the aliphatic bis(ynone)s produced a polymer containing both *E*- and *Z*-units[230] (Scheme 1.33).



Scheme 1.33

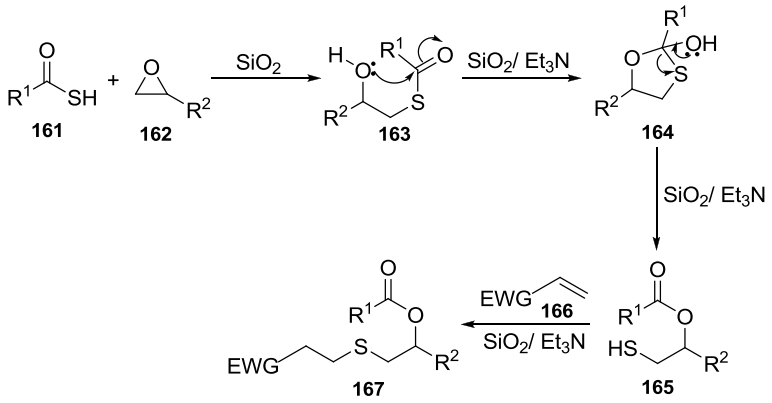
Biodegradable and inexpensive deep eutectic solvents[231-233] offer an efficient and convenient ionic reaction medium for the thia-Michael addition with *in situ* generation of *S*-alkylisothiouronium salts in place of thiols without the urea by-product segment. It provides an odorless and an atom-economic method for the preparation of β-keto sulfides via the one-pot reaction of thiourea, alkyl halides, and electron-deficient olefins in a choline chloride based deep eutectic solvent, under safe and eco-friendly conditions. Proposed mechanism for this green, thia-Michael addition involves the reaction of alkyl halide **154** with thiourea affords the isothiouronium salt **156**, which upon basic hydrolysis in the presence of NaOH generates the thiolate **158** and urea that acts as one of the components of the deep eutectic solvent **157**. The thiolate ion undergo *in situ* reaction with a Michael acceptor **159** to generate the carbon–sulfur bond (Scheme 1.34).[234]



Scheme 1.34

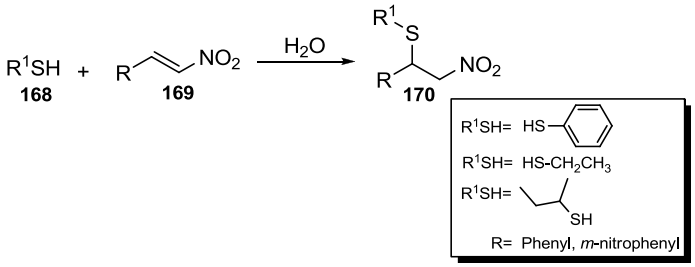
Silica gel catalysed regioselective addition of thio acid to the non-substituted carbon atom of the terminal epoxide produces the corresponding β-hydroxy thioester. β-hydroxythioester **163** undergo acyl group transfer from sulfur to the oxygen atom of the epoxide to form β-acyloxy mercaptans **165**; this immediately undergo Michael addition reaction with the electron-deficient alkene **166** (Scheme 1.35). It represents an efficient, straightforward, and high yielding procedure for the one-pot preparation of thia-Michael adducts of β-acyloxy mercaptans using thio acids, epoxides, and electron deficient alkenes under solvent-free conditions and in the presence of silica gel/Et_3N combined catalyst.[235] This method is important because it provides a short

synthetic route to achieve the corresponding thia-Michael adducts of non-commercial mercaptans using readily available substrates.



Scheme 1.35

Extensive research is going on for the development of green organic chemistry using water as the reaction medium.[236-239] Saidi, M. R. *et al.* have reported an efficient, novel, and green procedure for the Michael-type addition of thiols to activated unsaturated bonds in water without using any catalyst at room temperature in excellent yields. Michael addition reaction of aliphatic and aromatic thiols with nitroolefins results in the formation of nitrothio compounds under aqueous conditions (Scheme 1.36). The metal-free and nonhazardous experimental conditions, room-temperature operation, ease of reaction, short reaction times, and high yields are advantages of this method.[240]



Scheme 1.36

1.6. Diels-Alder Reaction

Diels–Alder reaction is a [4+2] cycloaddition reaction between a conjugated diene and a substituted alkene, commonly termed the dienophile, to form a substituted cyclohexene system. It was first described by Otto Paul Hermann Diels and Kurt Alder in 1928. It is one of the most fundamental and useful reactions in the field of the synthetic organic chemistry. For this work Otto Diels and Kurt Alder were awarded the Nobel Prize in Chemistry in 1950.[241-244] Diels-Alder reaction is one of the major synthetic strategies employed to generate bicyclic compounds.[245] These bicyclic compounds are of great importance since they constitute the basic structural framework of several compounds which are used as potential therapeutic agents against HIV,[246] anticancer drugs,[247] antithrombotic compounds,[248] therapeutic agents for diseases[249] of the central nervous system etc.

Diels–Alder reaction is widely used to construct a six-membered ring with upto four stereogenic centers in regio- and stereo-controlled pathways. In fact, anomeric effect, where

applicable, can provide additional stereocontrol. Thus, Diels-Alder reaction is an efficient route for the formation of carbon–carbon, carbon–heteroatom and heteroatom–heteroatom bonds in organic synthesis.[250] 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.

According to relative energies of the frontier molecular orbitals (FMOs) of the diene and the dienophile in the Hückel molecular orbital model, Diels-Alder reactions can be classified into two types of concerted suprafacial [$\pi4_s + \pi2_s$] cycloadditions: (i) the normal and (ii) inverse-electron-demand Diels-Alder reactions.[251,252] Based on Woodward-Hoffmann rules, both the reactions are thermally allowed.[253,254] Frontier molecular orbital theory predicts that the normal [$\pi4_s + \pi2_s$] cycloaddition could be controlled by a $HOMO_{diene}$ - $LUMO_{dienophile}$ interaction between electron-rich dienes and electron-deficient dienophiles whereas in inverse-electron-demand Diels-Alder reaction the $HOMO_{dienophile}$ - $LUMO_{diene}$ interaction is dominated. Wooward-Hoffmann rules give an idea about the transition states of Diels-Alder addition and it can have diradicaloid as well as zwitterionic transition states.[253]

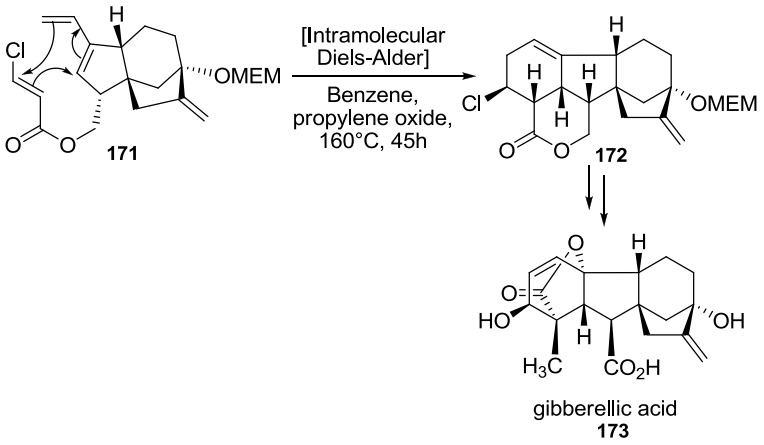
Stereoselectivity of Diels-Alder cycloaddition reaction shows that the endo adduct is stabilized by secondary orbital interactions in the transition state (TS), while the regioselectivity is controlled by both steric and electronic effects.[250] The Alder rule

of maximum accumulation of unsaturation has stimulated a number of evidences including stabilization of the endo transition state of Diels-Alder reactions by (i) inductive (van der Waals or dipolar) forces,[255,256] (ii) charge transfer,[257] (iii) favorable geometry for overlap,[258] (iv) secondary bonding forces[259] and (v) secondary orbital interactions.[260-262] The Diels-Alder reaction requires a ciscoid 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.[263-265]

For enantioselective Diels-Alder reactions, chiral catalysts play a key role in the reactivity and enantioselectivity. Chiral Lewis acid catalyzed asymmetric reactions represent the most powerful methods to afford optically active compounds.[266] Like acids, bases,[267] copper salts[268] and enzymes[269] are also used to catalyse the Diels-Alder reaction. In homo Diels-Alder reaction carbon-carbon bond formation takes place whereas in hetero Diels-Alder reaction either the diene or the dienophile contains a heteroatom, results in the formation of heterocycles.[270,271] Many studies reveal that the rate of the reaction depends on the solvent polarity, concentration and pressure of the reaction medium and also on the electron densities of the two pairs of carbons involved in the addition reaction.[272-274]

Intramolecular Diels-Alder cycloaddition is a Diels–Alder reaction in which the diene and the dienophile are in the same molecule. This cycloaddition reaction is extremely useful for the formation of naturally occurring polycyclic rings with a great deal

of stereoselectivity. One of the steps in the total synthesis of gibberellic acid (Scheme 1.37) is intramolecular Diels-Alder reaction which is carried out by E. J. Corey in 1978.[275] Intramolecular Diels-Alder reaction is of two type, Type I and Type II. Type I reaction means tether is attached at 4-position of the diene and in type II reaction the tether is attached at 3-position of diene[276,277] (Figure 1.).



Scheme 1.37

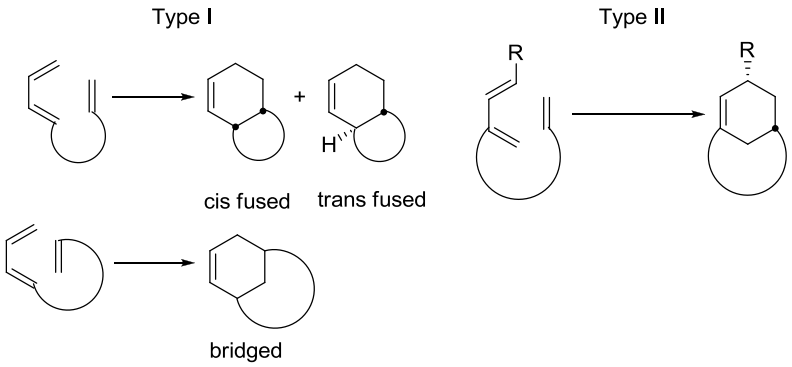
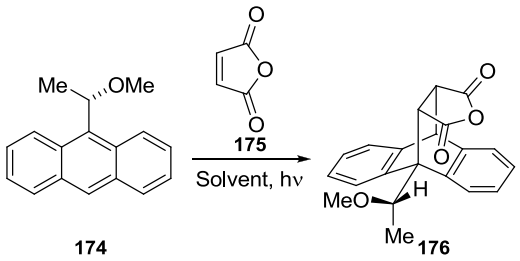


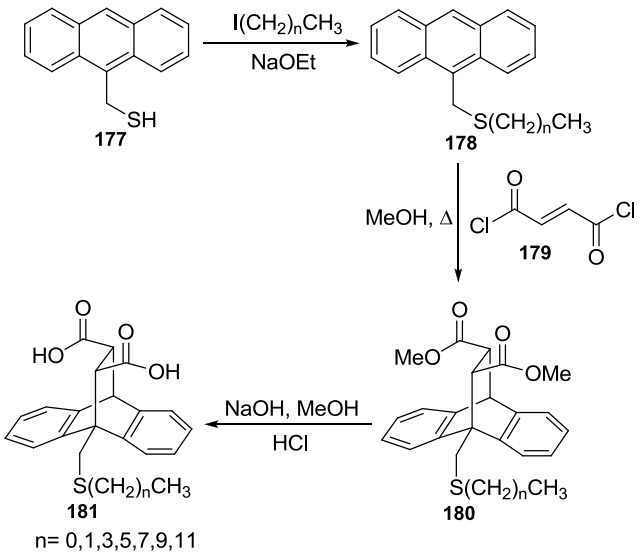
Figure 1.1

Anthracene undergo efficient Diels–Alder reaction with alkenes under thermal and photochemical conditions[250,274,278(a-e)] to give stable adducts which can be easily reverted to the original anthracene and alkene by flash vapour pyrolysis.[278f] The anthryl ring system acts as a powerful stereodirecting group[279] and this lends anthracene to being a useful framework for the development of photoactivated chiral auxiliary. Based on these facts chiral acrylates add to anthracene with excellent levels of diastereoselectivity.[280] A mono-substituted anthryl carbinol derivative can be easily accessed in non-racemic form by asymmetric reduction of a ketone precursor. The enantiomerically enriched chiral anthryl carbinol derivative **176** was prepared in 87% ee by asymmetric reduction in the presence of the catalyst (1*R*)-amino-(2*S*)-indanol. This chiral auxiliary undergo photoinduced Diels–Alder addition with maleic anhydride **175** under different solvents. In all cases no side products were formed and only a single diastereomer was obtained (Scheme 1.38). Under thermal conditions also the same product is formed and no side products were obtained. But the photoinduced Diels-Alder reaction is more efficient than the corresponding thermal or copper catalysed conditions.[281]



Scheme 1.38

Diels-Alder adduct of fumaric acid derivative and substituted anthracenes[282] achieves the unusual amphiphilic topology. In its doubly ionized form, the anthracene unit has a concave nonpolar face defined largely by the surfaces of the aromatic rings that are distal to the carboxylate-bearing bridge and a convex polar face dominated by the two carboxylate groups. Gellman *et al.* have described the preparation and characterization of a new series of amphiphiles **181** (Scheme 1.39).[283]



Scheme 1.39

1.7. Outline of the Research Problem and its Importance

From the literature survey it is clear that sulfides undergo efficient electron transfer reactions involving one electron transfer, two electron transfer and Diels-Alder reactions depending on the substrate structure and nature of the solvents, concentration and temperature. Our idea was to examine solvent dependency and effects of concentration and temperature on one electron transfer, two electron transfer and Diels-Alder reactions in sulfides. For this study we have selected (anthracen-9-yl)methyl sulfides. These anthracenemethyl sulfides can potentially undergo one electron transfer, two electron transfer and Diels-Alder reactions with suitable electron acceptors. For studying the effect of substituents on the electron acceptors in the above reaction we have selected three types of dienophiles having different electron withdrawing character *viz* dimethyl acetylenedicarboxylate (DMAD), dibenzoylacetylene (DBA) and dibenzoylethylene (DBE). For studying the solvent dependency in the reaction of sulfides with electron acceptors we have selected nonpolar, polar-aprotic and polar protic solvents. We propose to examine competing one electron transfer, Michael type addition and Diels-Alder reaction of anthracenemethyl sulfides and to unravel how these competitng reactions depend on substrate structure, concentration and solvent used in the reaction.

Furthermore, photoinduced electron transfer reactions can be studied by the acceptor-spacer-donor type anthracenemethyl sulfides (Figure 1.2). Diels-Alder adducts formed in the reaction of these anthracenemethyl sulfides with electron deficient acetylenes such as DBA and DMAD are sulfide appended dibenzobarrelenes (Figure 1.3). Generally sulfides are efficient quenchers of singlet excited states. These sulfide appended dibenzobarrelenes proved ideal systems to examine competition between known barrelene photochemistry and putative competing electron transfer mediated quenching that can lead to hitherto unexplored phototransformations of barrelenes.

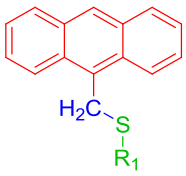


Figure 1.2

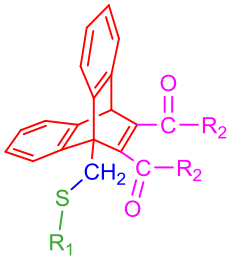


Figure 1.3

1.8. Objectives

1. Synthesis of (anthracen-9-yl)methyl sulfides.

2. Synthesis of dienophiles.
   - ❖ Synthesis of dibenzoylethylene
   - ❖ Synthesis of dibenzoylacetylene

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

4. Explore the photoinduced electron transfer reactions in (anthracen-9-yl)methyl sulfides.

5. Examine the photoinduced electron transfer reactions in anthracenemethyl sulfide derived dibenzobarrelenes.

6. Deducing mechanisms for the observed thermal and photochemical reactions.

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CHAPTER 2

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

2.1. Abstract

This chapter deals with the synthesis of several (anthracen-9-yl)methyl sulfides that could potentially undergo competing one electron transfer, two electron transfer (Michael addition) and Diels-Alder reactions with suitable electron acceptors.

2.2. Introduction

Organosulfur compounds are important intermediates for specialized organic synthesis.[1-3] These compounds are well known for their radical chemistry under thermal and photochemical conditions.[4-12] Sulfur-centred radicals and radical ions play unique roles in diverse areas of chemistry. Organic sulfides undergo fast one electron oxidation reactions, because of their low ionization potentials. Thus, by chemical oxidation with suitable oxidants[13-15], by electrochemical oxidation[16,17] or by photochemical oxidation[18-20]

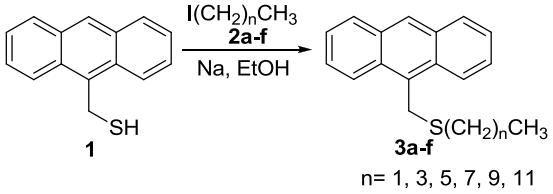
an electron from the lone pair on the sulfur atom can be removed to form the corresponding molecular radical cations, which can be utilized for exploring the mechanisms of electron transfer quenching of excited states as well as for observing the fate of the sulfur radicals.[21-25] A special feature of dialkyl sulfide radical cations is that it forms relatively stable "dimer" radical cations by its reaction with neutral parent molecule. Here the two sulfur atoms are held together by a two-center-three-electron bond.[26] The reactivity of radical cations from aromatic sulfides is expected to be influenced by the degree of spin delocalization in the aromatic ring, for which the conformation of the radical cation is important.[27] But it is noted that spin delocalization should reduce the tendency of the radical cation to form dimers.[28]

Anthracene and its derivatives are excellent dienes and are generally known to undergo Diels-Alder reactions under thermal and photochemical conditions with a variety of dienophiles across 9 and 10 positions.[29] This was the key step for the synthesis of some antidepressant drugs and antianxiety drugs such as benzoctamine, maprotiline and a homologues of these compounds bishomobenzoctamine and bishomomaprotiline.[30,31] In the past two decades the thiol-Michael addition reaction or conjugate addition of thiols or thiolate anions, to electron-deficient C=C bonds has garnered significant attention, due to its facile, powerful nature.[32] Hence we selected (anthracen-9-yl)methyl sulfides for studying competitive reactions including one electron transfer, Michael addition and Diels-Alder reaction with suitable dienophiles. Here

the sulfide moiety is linked to an anthracene ring through a methylene spacer. The methylene spacer will effectively shut the electronic communication between sulfide and anthracene component in the ground state. Sulfide part of (anthracen-9-yl)methyl sulfides can easily undergo one electron transfer and Michael addition reactions whereas anthracene part undergo Diels-Alder reaction with suitable electron acceptors. Thus, these molecules can react independently as an anthracene or a sulfide through multiple reaction pathways.

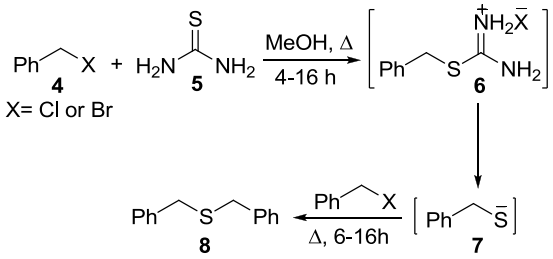
We synthesized a series of unsymmetrical (anthracen-9-yl)methyl sulfides using either a newly developed one-pot reaction between 9-anthracenemethanol, thiourea and the corresponding alkyl halide or by the base promoted one-pot reductive coupling of tosylhydrazones with thiols.

The conventional method used for the synthesis of organic sulfides involves the reaction of a thiol (or disulfide) with a halide in the presence of a strong base.[33] This method is robust but requires handling of malodorous thiols and reactive halides that are difficult to handle. Moreover, not many thiols are commercially available. There are reports on the synthesis of (anthracen-9-yl)methyl alkyl sulfides **3a-f** by the reaction of the corresponding alkyl iodide **2a-f** with 9-anthracenemethanethiol (**1**) in presence of sodium metal under inert condition (Scheme 2.1).[34] The reaction condition is somewhat tedious because of the use of malodorous thiol, reactive sodium metal and inert atmosphere in the procedure.



Scheme 2.1

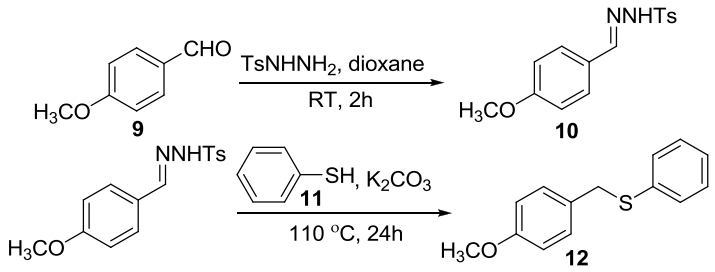
A one pot synthesis of symmetrical and unsymmetrical benzyl sulfides from benzyl halides using thiourea has been reported. It is shown that the isolation of the intermediate thiol or isothiouronium salt **6** is not required making this procedure more conveneient. The sulfide ion **7** generated from benzyl halide reacts *in-situ* with a second molecule of benzyl halide, thereby avoiding the need for isolation of the malodorous thiol (Scheme 2.2).[35] But the synthetic scope of this reaction is limited to symmetrical sulfides. Availability and stability of benzyl halides also are major hurdles.



Scheme 2.2

Many reports on the formation of aryl and alkyl sulfides using cross-coupling reactions of aryl or alkyl halides with various nucleophilic compounds are available, but these reactions require

more forcing conditions such as use of transition metal catalyst[36-40] or photochemical activation.[41] High cost and toxicity of some transition metal catalysts and ligands restrict their applications in large-scale processes. Recent modifications such as metal free reactions have shown the same levels of efficiency as metal-catalysed reactions.[42] Ding *et al.* reported the synthesis of substituted benzyl phenyl sulfides **12** via the metal free reductive coupling of tosyl hydrazones **10** with substituted benzene thiols **11** (Scheme 2.3).[43]



Scheme 2.3

2.3. Results and Discussion

For studying the competing reactions of (anthracen-9-yl)methyl sulfides with suitable electron acceptors in different solvents and under different conditions, we required ready access to to multigram quantities of the required sulfides **13a-e** (Figure 2.1). Conventional methods available for the synthesis of sulfides did not satisfy our requirements. So we developed highly efficient and scalable one pot reaction using readily accessible 9-

anthracenemethanol, thiourea and the corresponding alkyl halide (Scheme 2.4) adapting a reported procedure for the synthesis of thiols.[44] Conspicuous advantage of this procedure is avoidance of direct use of thiols. (Anthracen-9-yl)methyl phenyl sulfide (**13f**, Figure 2.1) was prepared by the reductive coupling between 9-anthraldehyde tosylhydrazones and benzenethiol following the protocol developed by Ding.[43]

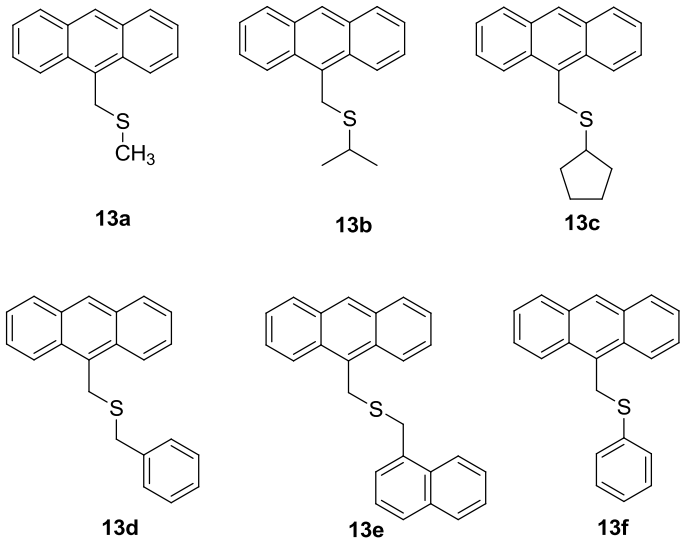
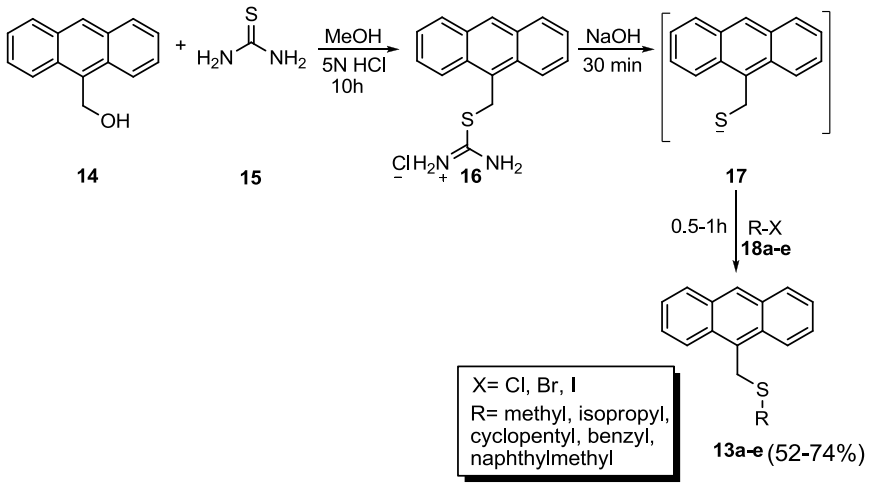


Figure 2.1. Selected (anthracen-9-yl)methyl sulfides

Anthracenemethyl thiol is conveniently prepared by the reaction between 9-anthracenemethanol and thiourea.[45] We reasoned that the thiolate ion generated as an intermediate can be intercepted by a suitable alkyl halide to give the corresponding sulfide in a one pot reaction. Applying this strategy, we synthesized (anthracen-9-yl)methyl alkyl sulfides **13a-e** by the one

pot reaction of 9-anthracenemethanol (**14**), thiourea (**15**) and the corresponding alkyl halide **18a-e**. Reaction of **14** with **15** under acidic conditions affords the isothiouronium salt **16** which upon treatment with a strong base generates the thiolate **17**. This intermediate is further reacted *in situ* with a series of alkyl halides **18a-e** to generate the required (anthracen-9-yl)methyl alkyl sulfides **13a-e**. Here the isolation of intermediate thiol or isothiouronium salt is not required, thereby significantly simplifying this synthetic method. The reaction took place in good yields (Table 2.1). Steps involved in the synthesis of (anthracen-9-yl)methyl alkyl sulfides **13a-e** is presented in Scheme 2.4.



Scheme 2.4

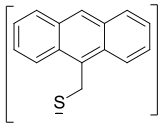
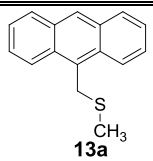
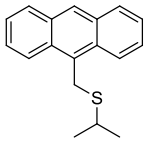
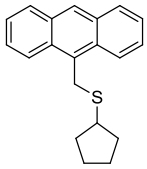
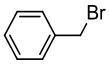
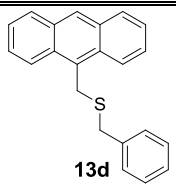
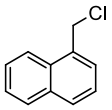
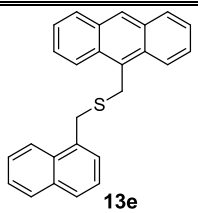
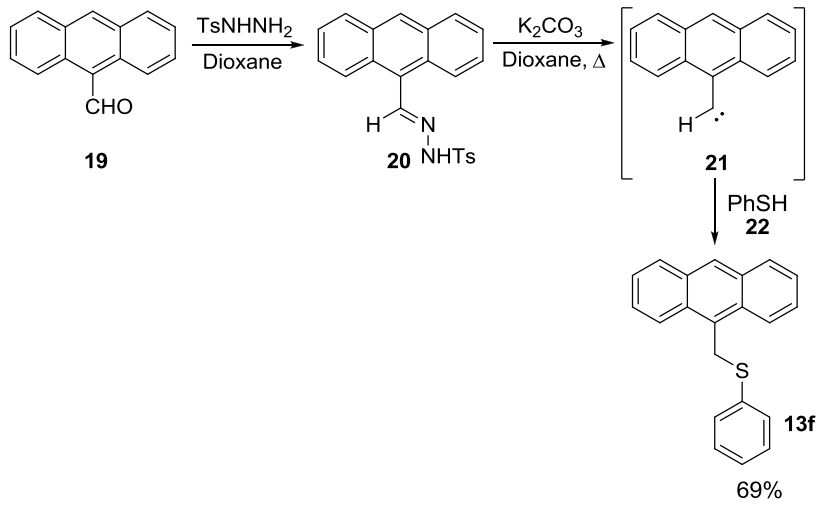
Entry	Alkyl Halide R-X	Thiolate intermediate	Product	Yield (%)	Time
1	CH_3I **18a**	 **17**	 **13a**	74	30 min.
2	 **18b**		 **13b**	59	30 min.
3	 **18c**		 **13c**	74	1 h
4	 **18d**		 **13d**	61	30 min.
5	 **18e**		 **13e**	52	1h

Table 2.1. List of (anthracen-9-yl)methyl sulfides synthesized using a one pot reaction from 9-anthracenemethanol, thiourea and alkyl halide.

As can be inferred from the mechanism presented in Scheme 2.4, phenols cannot react with thiourea to generate isothiouronim salts analogous to **16**. Additionally, the reaction

fails with halobenzenes. Thus a major limitation of the procedure shown in Scheme 2.4 is that this method is not suitable for the preparation of aryl sulfides such as **13f**. Hence, we adopted the metal free reductive coupling reaction reported by Ding[43] for the generation of aryl sulfides. Reaction of benzene thiol (**22**) with tosylhydrazone **20** derived from 9-anthraldehyde (**19**) proceeded smoothly to give (anthracen-9-yl)methyl phenyl sulfide (**13f**) in high yields (Scheme 2.5). Aryl thiols are less volatile and hence are less malodorous in nature. The proposed reductive coupling mechanism involves the initial generation of an intermediate carbene **21** via the base promoted thermal decomposition of tosylhydrazone[46,47] **20**. Insertion of incipient carbene **21** into the S-H bond of benzene thiol (**22**), results in the formation of (anthracen-9-yl)methyl phenyl sulfide (**13f**). Structure of **13a-f** was established on the basis of analytical and spectral data. ^{1}H and ^{13}C NMR spectra of these compounds were in agreement with the expected structure and they exhibited acceptable elemental analysis and mass spectral data.



Scheme 2.5

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 silica gel (*Spectrochem Chemicals*, 60-120 mesh). 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 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 on a *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. All the required starting materials are commercially available and were used as received.

2.4.2. 9-Anthracenemethanol:

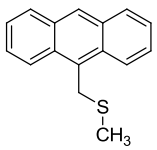
9-Anthracenemethanol (**14**) was prepared using a known procedure[48] (60%, mp 158-162 °C).

2.4.3. Synthesis of (Anthracen-9-yl)methyl sulfides:

2.4.3.1. (Anthracen-9-yl)methyl methyl sulfide (13a).

To a solution of 9-anthracenemethanol (**14**) (2g, 9.6 mmol) in 15 mL of methanol, thiourea (**15**) (1.46g, 19.2 mmol) and 10 mL of 5N HCl were added and the mixture was stirred at RT for 10h. To this mixture, NaOH pellets (1.15g, 28.8 mmol) were added and the mixture was stirred vigorously for 15 minutes. On addition of NaOH, yellow color of the solution turned into grey. At this point, 1.1 equiv. of methyl iodide (0.66 mL, 10.5 mmol) was added and the mixture was stirred for 30 min. After the completion of the reaction, the reaction mixture was poured into water and extracted with dichloromethane. Organic layer was separated, washed with water and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the product obtained was passed through a silica gel column to purify (anthracen-9-yl)methyl methyl sulfide **13a**. The solid obtained upon removal of solvent was purified by recrystallization from a mixture (1:3) of hexane and dichloromethane.

Compound 13a



Yellow solid.

mp: 110 °C.[34]

IR ν_{max} (KBr): 3055, 2958, 2846, 1619, 1598, 1392, 719 cm^{-1}.

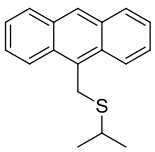
^{1}H NMR ($CDCl_3$): δ 8.30-7.38 (m, 9H), 4.65 (s, 2H), 2.06 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 130.6, 128.9, 128.3, 128.2, 126.2, 125.1, 124.0, 123.2, 37.5, 17.2.
MS: *m/z* 238 (M^+), 191.
Elemental analysis calculated for
$C_{16}H_{14}S$: C, 80.63; H, 5.92; S, 13.45.
Found: C, 80.58; H, 5.85; S, 13.39.

2.4.3.2. (Anthracen-9-yl)methyl isopropyl sulfide (13b).

To a solution of 9-anthracenemethanol (**14**) (2g, 9.6 mmol) in 15 mL of methanol, thiourea (**15**) (1.46g, 19.2 mmol) and 10 mL of 5N HCl were added and the mixture was stirred at RT for 10h. To this mixture, NaOH pellets (1.15g, 28.8 mmol) were added and the mixture was stirred vigorously for 15 minutes. On addition of NaOH, yellow color of the solution turned into grey. To this mixture, 1.1 equiv. of isopropyl iodide (1.05 mL, 10.5 mmol) was added and the mixture was stirred for 30 min. After the completion of the reaction, the reaction mixture was poured into water and extracted with dichloromethane. Organic layer was separated, washed with water and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the product obtained was passed through a silica gel column to purify (anthracen-9-yl)methyl isopropyl sulfide **13b**. The solid obtained upon removal of solvent was purified by recrystallization from a mixture (1:3) of hexane and dichloromethane.

Compound 13b Yellow solid.



mp: 62-64 °C.

IR ν_{max} (KBr): 3053, 2957, 2858, 1620, 1597, 1384, 722 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 8.31-7.37 (m, 9H), 4.68 (s, 2H), 3.19- 3.09 (m, 1H), 1.37 (d, 6H, *J*= 6.8 Hz).

^{13}C NMR ($CDCl_3$): δ 130.6, 128.9, 128.3, 128.2, 126.2, 125.1, 124.0, 123.2, 35.7, 26.9, 22.6.

MS: *m/z* 266 (M^+), 191.

Elemental analysis calculated for

$C_{18}H_{18}S$: C, 81.15; H, 6.81; S, 12.04.

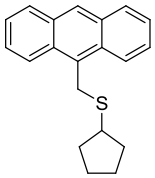
Found: C, 81.07; H, 6.76; S, 11.99.

2.4.3.3. (Anthracen-9-yl)methyl cyclopentyl sulfide (13c).

At RT, a solution of 9-anthracenemethanol (**14**) (2g, 9.6 mmol) in 15 mL of methanol, thiourea (**15**) (1.46g, 19.2 mmol) and 10 mL of 5N HCl were stirred in a magnetic stirrer for 10h. To this mixture, NaOH pellets (1.15g, 28.8 mmol) were added and the mixture was stirred vigorously for 15 minutes. On addition of NaOH, yellow color of the solution turned into grey. To this mixture, 1.1 equiv. of cyclopentyl bromide (1.13 mL, 10.5 mmol) was added and the mixture was stirred for one hour. After the completion of the reaction, the reaction mixture was poured into water and extracted with dichloromethane. The organic layer was collected, washed with water and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the product

obtained was passed through a silica gel column to purify (anthracen-9-yl)methyl cyclopentyl sulfide **13c**. The solid obtained upon removal of solvent was purified by recrystallization from a mixture (1:3) of hexane and dichloromethane.

Compound 13c



Yellow solid.

mp: 66-68 °C.

IR ν_{max} (KBr): 3084, 2952, 2857, 1619, 1598, 1399, 723 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 8.30-7.36 (m, 9H), 4.68 (s, 2H), 3.29-3.22 (m, 1H), 2.05- 1.98 (m, 2H), 1.73-1.69 (m, 2H), 1.63-1.51 (m, 4H).

^{13}C NMR ($CDCl_3$): δ 130.6, 128.9, 128.6, 128.1, 126.1, 125.0, 123.9, 123.2, 44.1, 33.2, 33.0, 28.1, 24.0, 23.8.

MS: *m/z* 292 *(M^+)*, 191.

Elemental analysis calculated for

$C_{20}H_{20}S$: C, 82.14; H, 6.89; S, 10.96.

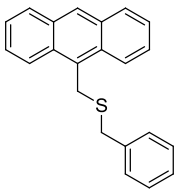
Found: C, 82.08; H, 6.81; S, 10.89.

2.4.3.4. (Anthracen-9-yl)methyl benzyl sulfide (13d).

A solution of 9-anthracenemethanol (**14**) (2g, 9.6 mmol) in 15 mL of methanol, thiourea (**15**) (1.46g, 19.2 mmol) and 10 mL of 5N HCl were mixed and stirred at RT for 10h. To this mixture, NaOH pellets (1.15g, 28.8 mmol) were added and the mixture was stirred vigorously for 15 minutes. When NaOH was added, yellow color of the solution turned into grey. To this mixture, 1.1 equiv. of benzyl bromide (1.25 mL, 10.5 mmol) was added and the

mixture was stirred for 30 min. After the completion of the reaction, the reaction mixture was poured into water and extracted with dichloromethane. The organic layer was separated, washed with water and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the product was column chromatographed using silica gel to purify (anthracen-9-yl)methyl benzyl sulfide **13d**. The solid obtained upon removal of solvent was purified by recrystallization from a mixture (1:3) of hexane and dichloromethane.

Compound 13d



Yellow solid.

mp: 74-76 °C.

IR ν_{max} (KBr): 3061, 2911, 1599, 1384, 735, 697 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 8.36-7.32 (m, 14H), 4.60 (s, 2H), 3.89 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 136.4, 130.5, 129.1, 128.5, 128.1, 127.5, 127.1, 126.8, 126.5, 125.1, 124.1, 123.4, 42.8, 35.9.

MS: *m/z* 314 (M^+), 191, 91.

Elemental analysis calculated for

$C_{22}H_{18}S$: C, 84.03; H, 5.77; S, 10.20.

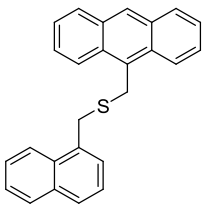
Found: C, 83.92; H, 5.73; S, 10.12.

2.4.3.5. (Anthracen-9-yl)methyl naphthylmethyl sulfide (13e).

Thiourea (**15**) (1.46g, 19.2 mmol) and 10 mL of 5N HCl were added to a solution of 9-anthracenemethanol (**14**) (2g, 9.6 mmol) in 15 mL of methanol, and were stirred at RT for 10h. To

this mixture, NaOH pellets (1.15g, 28.8 mmol) were added and the mixture was stirred vigorously for 15 minutes. Upon NaOH addition, yellow color of the solution turned into grey. To this mixture, 1.1 equiv. of 1-(chloromethyl)naphthalene (1.58 mL, 10.5 mmol) was added and the mixture was stirred for one hour. After the completion of the reaction, the reaction mixture was poured into water and extracted with dichloromethane. The organic layer was separated, washed with water and dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the product was column chromatographed using silica gel to purify (anthracen-9-yl)methyl naphthylmethyl sulfide **13e**. The solid obtained upon removal of solvent was purified by recrystallization from a mixture (1:3) of hexane and dichloromethane.

Compound 13e



Yellow solid.

mp: 94-96 °C.

IR ν_{max} (KBr): 3080, 3046, 2931, 2860, 1598, 1380, 779, 716 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 8.35-7.32 (m, 16H), 4.65 (s, 2H), 4.33 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 134.2, 133.5, 131.6, 131.5, 130.1, 129.1, 128.8, 128.3, 127.4, 127.3, 126.1, 126.0, 125.9, 125.1, 125.0, 124.1, 35.3, 29.0.

MS: *m/z* 364 *(M^+)*, 191, 141.

Elemental analysis calculated for

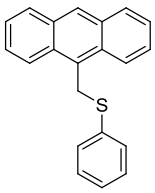
$C_{26}H_{20}S$: C, 85.67; H, 5.53; S, 8.80.

Found: C, 85.58; H, 5.46; S, 8.76.

2.4.3.6. (Anthracen-9-yl)methyl phenyl sulfide (13f).

To a solution of 9-anthraldehyde (**17**) (1.0 g, 4.8 mmol) in 5 mL of dioxane, tosyl hydrazide (1.8g, 9.6 mmol) was added and the mixture was stirred for 1 h. To this mixture benzene thiol (**21**) (0.98 mL, 9.6 mmol) and K_2CO_3 (2g, 14.4 mmol) were added and the mixture was stirred at 100 °C for 2h. After completion of the reaction, as indicated by TLC, the reaction mixture was cooled to room temperature. To this mixture, ethyl acetate (25 mL) was added and the organic phase was washed with brine, dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography on silica gel to yield **13f**.

Compound 13f



Yellow solid.

mp: 100-102 °C.

IR ν_{max} (KBr): 3061, 2951, 2859, 1597, 1384, 729, 686 cm^{-1}.

^{1}H NMR ($CDCl_3$):- δ 8.42-7.22 (m, 14H), 5.12 (s, 2H).

^{13}C NMR ($CDCl_3$):- δ 137.4, 131.5, 130.1, 129.9, 129.2, 129.0, 127.6, 126.5, 126.2, 125.1, 124.1, 32.1.

MS: *m/z* 300 *(M^+)*, 191.

Elemental analysis calculated for

$C_{21}H_{16}S$: C, 83.96; H, 5.37; S, 10.67.

Found: C, 83.91; H, 5.33; S, 10.58.

2.5. References

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CHAPTER 3

REACTIONS OF (ANTHRACEN-9-YL)METHYL SULFIDES WITH SUITABLE DIENOPHILES IN DIFFERENT SOLVENTS

3.1. Abstract

In this chapter, we describe solvent dependent diverse reactivity of (anthracen-9-yl)methyl sulfides with suitable dienophiles. Diversity in reactivity is attributed to competition between one electron transfer, two electron transfer and Diels-Alder reaction of these sulfides with different electron deficient dienophiles. We have proposed plausible mechanisms to account for various reactions observed by us.

3.2. Introduction

Competing reactions are those in which compounds react with each other and/or decompose concomitantly in multiple modes to give different products. Several competing reactions involving competition between S_N2 and E2 mechanisms,[1-5] endothermic proton transfer competing with exothermic S_N2 channel,[6] one electron transfer versus nucleophilic attack,[7] competition between

monomolecular and bimolecular reactions[8] and free radical versus anionic cycloaromatization[9] reactions are well documented in literature. There are also competing electron transfer, proton abstraction, nucleophilic substitutions and base-induced elimination reactions in gas-phase reactions.[10,11] Several examples of competing photochemical transformations are also available in literature. Irradiation of cyclodextrin-bound benzoin methyl ether, benzoin ethyl ether, and benzoin isopropyl ether, for example, leads to a large change in product distribution when it is conducted in aqueous solution and in the solid state. In aqueous solution Norrish type II products compete with that of Norrish type I, and in the solid state, type II products constitute more than 90% of the product distribution.[12]

Recently we observed multiple pathways operating concurrently in the reaction between (anthracen-9-yl)methanamines and reactive acetylenes.[13-16] Depending on the nature of solvent, major pathway changes from single electron transfer to nucleophilic addition. In nonpolar and polar aprotic media, depending on substrate concentration, competition between one electron transfer and Diels-Alder reaction pathways were observed. In polar protic solvents, Michael type addition was the major pathway. With increasing concentration of reactants, cycloaddition pathway gained prominence in all solvents examined by us. These results prompted us to investigate similar competing reaction sequences with other suitable substrates. Since tertiary amines and organic sulfides have comparable ionization potential (~8.2 eV),[17]

we reasoned that (anthracen-9-yl)methyl sulfides also should give similar reactions with suitable dienophiles. In support of our assumption, it has already been reported that organic sulfides efficiently undergo fast one[18,19] and two electron[20-22] oxidation reactions, owing to their relatively low ionization potentials. (Anthracen-9-yl)methyl sulfides by virtue of being 9-substituted anthracenes are reactive dienes capable of undergoing Diels-Alder reaction with a variety of dienophiles.[23,24] Hence it is reasonable to assume that anthracenemethyl sulfides (**1-6**, Chart 3.1) also should undergo competing one electron transfer (*path **a***), two electron transfer (Michael type addition, *path **b***) and (4+2) cycloaddition reaction (Diels-Alder reaction, *path **c***) with suitable dienophiles such as dimethyl acetylenedicarboxylate (DMAD, **7a**, Chart 3.1), dibenzoylacetylene (DBA, **7b**, Chart 3.1) and dibenzoylethylene (DBE, **7c**, Chart 3.1) in different solvents (Scheme 3.1). All the three reactions (*path **a***, *path **b*** & *path **c***) are bimolecular reactions. It is clear that the transition state for single electron transfer reactions (*path **a***) are loosely bound whereas Diels-Alder reaction (*path **c***) requires tighter and better aligned transition state to proceed smoothly. On the other hand, a polar transition state is involved in Michael additions (*path **b***). Such polar transition states are stabilized by polar protic solvents. Thus, it may be expected that single electron transfer reactions and Diels-Alder reactions take precedence over Michael additions in nonpolar media whereas Michael addition is competitive in polar protic solvents. These considerations provided us challenging oppurtunities to examine

the competing reactions of (anthracen-9-yl)methyl sulfides (**1-6**) with suitable dienophiles (**7a-c**) as a function of several variables including solvent polarity, nature of solvent, nature of substrates and reaction temperature.

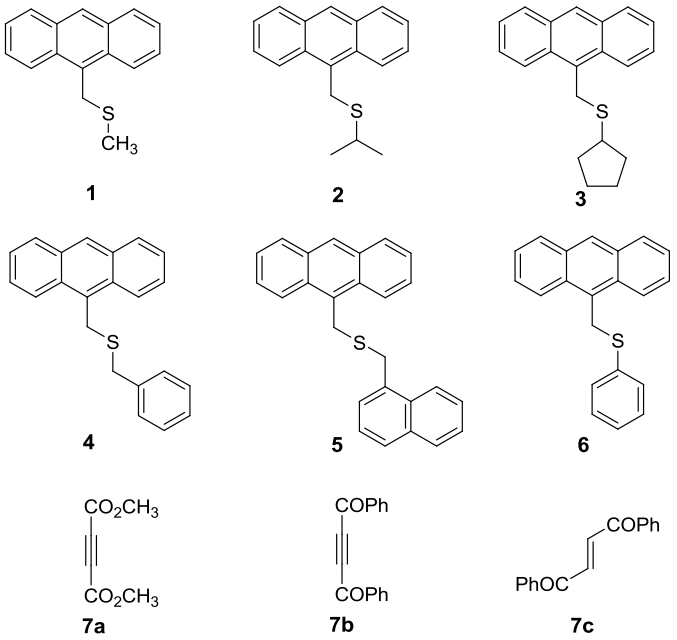
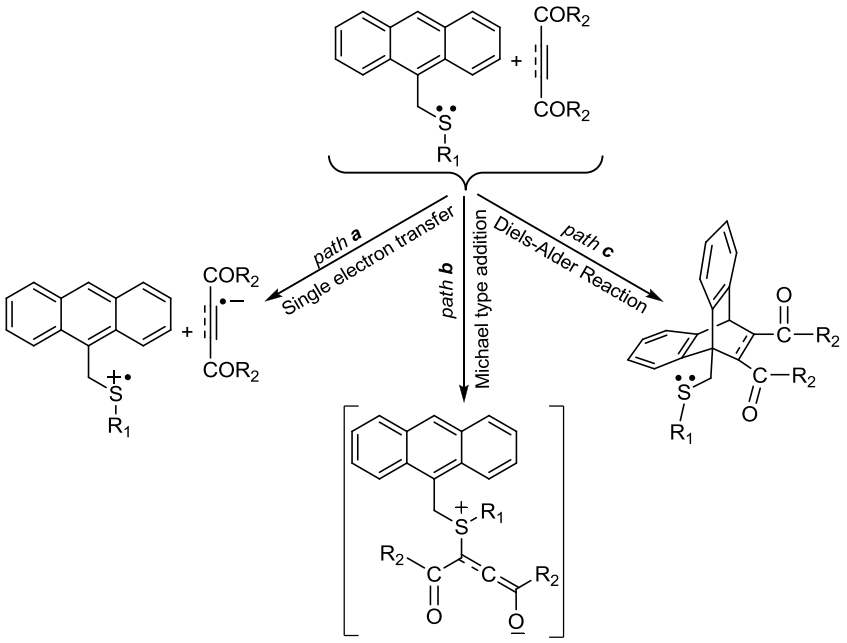


Chart 3.1. Selected (anthracen-9-yl)methyl sulfides and electron deficient dienophiles.



Scheme 3.1

3.3. Results and Discussion

For studying the effect of solvent, concentration and nature of substrates in the reaction between (anthracen-9-yl)methyl sulfides (**1-6**) and electron deficient dienophiles **7a-c**, we performed the reaction in different solvents under different concentrations of substrates. We selected three different types of solvents *viz* nonpolar solvent - xylene, polar aprotic solvents - DMF and acetonitrile and polar protic solvents - alcohol (methanol) and acid (acetic acid). In continuation we examined reactions with different dienophiles such as dimethyl acetylenedicarboxylate (DMAD), dibenzoylacetylene (DBA) and dibenzoylethylene

(DBE). As expected, product distribution changed under different conditions. However, a few products arising through (*i*) single electron transfer mediated transformations such as 9-methylanthracene[25] (**8**), 1,2-bis(9-anthracenyl)ethane[26-29] (**9**), lepidopterene[26,30-34] (**10**) 9-anthraldehyde[35] (**11**) and dimethyl 1-oxo-1*H*-benzo[*de*]anthracene-2,3-dicarboxylate (**12**), (*ii*) reaction with adventitious oxygen[36] such as 9,10-anthraquinone (**13**) and (*iii*) Diels Alder reaction ((**14-19**)**a**, (**14-19**)**b** & (**14-19**)**c**) were common in all reactions (Chart 3.2). In most cases, DBA underwent cyclotrimerization to yield hexabenzoylbenzene (**20**) and 1,2,4,5-tetrabenzoylbenzene (**21**).[37] DMAD underwent oligomerization and in a few cases the corresponding hexamer **22** could be isolated in very low yields[38] (Chart 3.3). In nonpolar and polar aprotic solvents we observed competition between one electron transfer and Diels-Alder pathways. Here Diels-Alder pathway is the major one. But in polar protic solvents: for DMAD, two electron transfer reaction is the major one and for DBA and DBE, Diels-Alder pathway competes over the other two.

We repeated the reaction of anthracenemethyl sulfides with dienophiles with ten fold decrease in concentration. In this case we observed similar results and there is no change in the reaction pathway. In contrast to dramatic concentration dependence observed in the reaction between anthracenemethanamines and acetylenes,[13,14] anthracenemethyl sulfide-electron acceptor reactions were unaffected by change in concentration. At lower concentration, reaction took much longer times to reach

completion. The observations and proposed mechanisms for reactions under various conditions are discussed below.

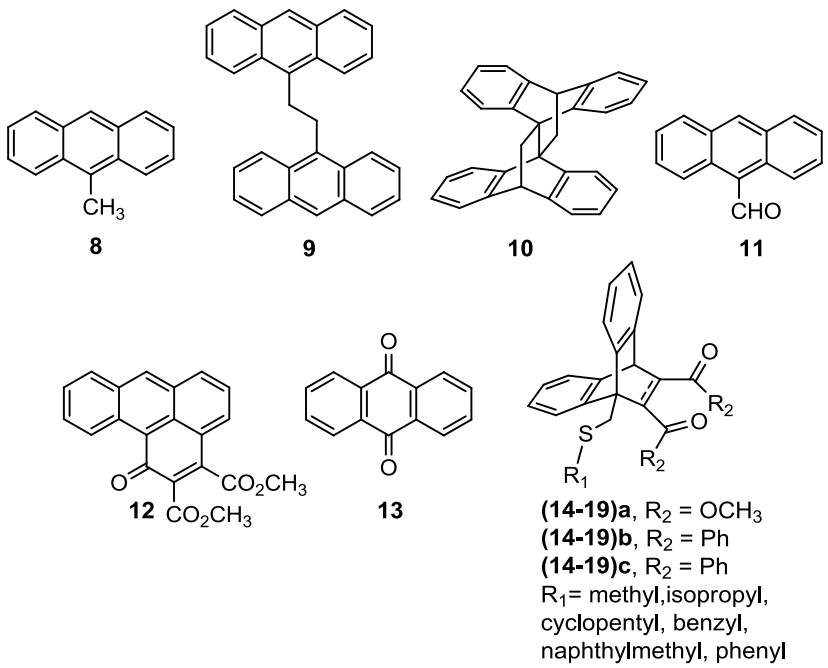


Chart 3.2. Common products formed in the reaction between **1-6** and electron deficient dienophiles **7a-c**.

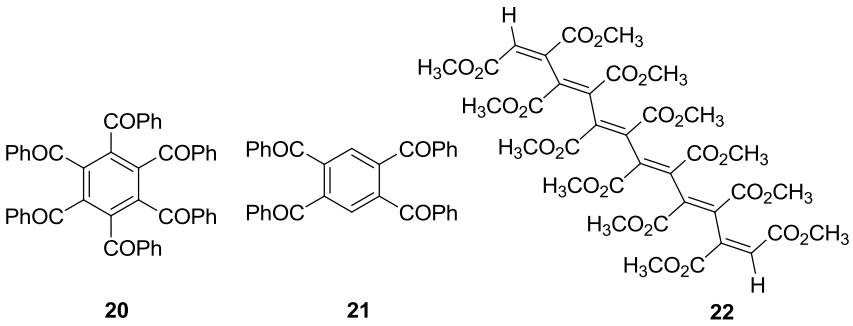


Chart 3.3. Oligomerization products of electron deficient dienophiles **7a** & **7b**.

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

3.3.1.1. Reactions in non-polar solvent: xylene

A 0.42 M solution of (anthracen-9-yl)methyl sulfides (**1-6**) was refluxed with 2 equivalents of DMAD (**7a**) in xylene. Diels-Alder adduct[23] **(14-19)a** was obtained in major amounts along with a variety of products including 9-methylanthracene (**8**), 1,2-bis(9-anthracenyl)ethane (**9**), lepidopterene (**10**) 9-anthraldehyde (**11**), dimethyl 1-oxo-1*H*-benzo[*de*]anthracene-2,3-dicarboxylate (**12**) and 9,10-anthraquinone (**13**) in minor to negligible amounts (Chart 3.2). The reaction was accompanied by high degree of DMAD oligomerization to give highly polar, intractable residue. However, hexamer **22** could be isolated in trace amounts (Chart 3.3). Details of yield of different products and time taken for the reaction are depicted in Table 3.1.

Sulfide	Reaction Time (h)	8 (%)	9 (%)	10 (%)	11 (%)	12 (%)	13 (%)	(14-19)a (%)	22 (%)
1	10	2	<1	<1	9	10	1	44	<1
2	20	<1	<1	<1	<1	11	2	67	<1
3	8	<1	<1	<1	<1	2	<1	70	<1
4	11	<1	<1	<1	<1	5	12	53	<1
5	20	<1	<1	<1	4	4	3	51	<1
6	17	<1	<1	<1	1	7	<1	42	<1

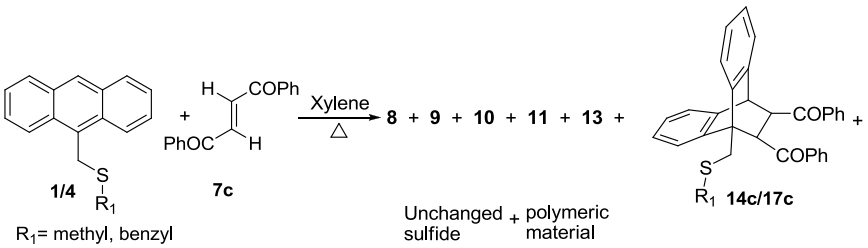
Table 3.1. Yield (%) of different products and time taken for the reaction of **1-6** with **7a** in xylene (0.42 M).

To study the effect of nature and reactivity of dienophiles, we repeated the reaction with DBA and DBE as electron deficient dienophiles. Similar results were obtained, but the product analogous to **12** was not formed when DBA (**7b**) and DBE (**7c**) were used as the electron deficient dienophiles. In the DBA reaction, cyclotrimerization products such as **20** and **21** were isolated in trace amounts. Details of yield of different products and time taken for the reaction between anthracenemethyl sulfides and DBA are depicted in Table 3.2. Also the reaction scheme for the reaction between (anthracen-9-yl)methyl sulfides (**1** & **4**) and DBE (**7c**) are shown in Scheme 3.2. Since the electron deficiency of DBE is comparatively lower than that of DMAD and DBA, the reaction between anthracenemethyl sulfides and DBE is very slow and also about 40-50% of starting materials remained unchanged in

the reaction. The yield (%) of different products obtained and the reaction time are shown in Table 3.3.

Sulfide	Reaction Time (h)	8 (%)	9 (%)	10 (%)	11 (%)	13 (%)	(14-19)b (%)	20 (%)	21 (%)
1	15	1	<1	<1	5	2	56	<1	<1
2	12	1	<1	<1	<1	5	76	1	<1
3	16	<1	<1	<1	3	7	64	<1	<1
4	20	<1	<1	<1	7	5	59	<1	<1
5	24	1	<1	<1	7	<1	61	2	<1
6	19	2	<1	<1	13	<1	63	<1	1

Table 3.2. Yield (%) of different products and time taken for the reaction of **1-6** with **7b** in xylene (0.42 M)



Scheme 3.2

Sulfide	Reaction Time (h)	8 (%)	9 (%)	10 (%)	11 (%)	13 (%)	14c/17c (%)	Unchanged 1/4 (%)
1	48	1	<1	<1	5	<1	34	42
4	48	<1	<1	2	3	<1	37	45

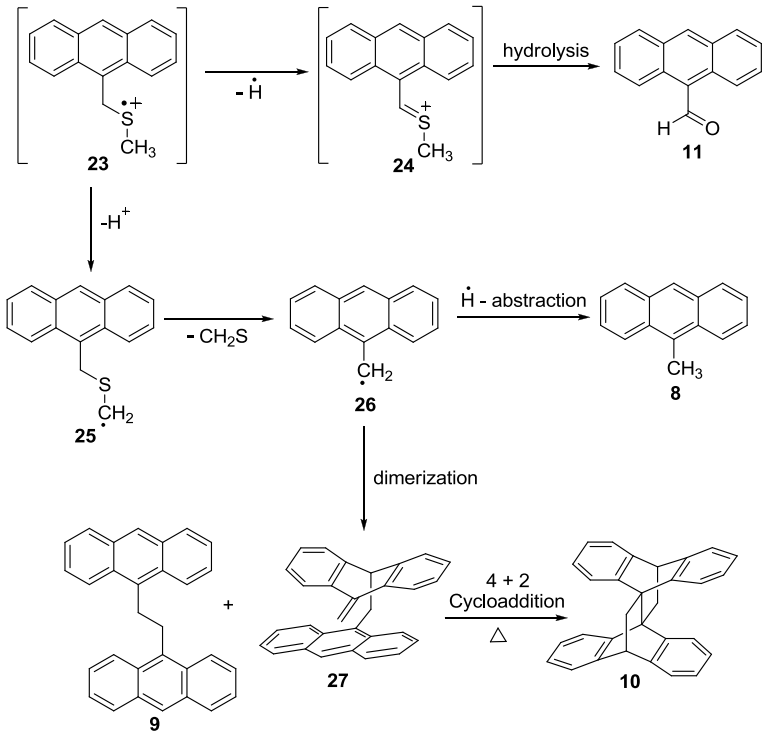
Table 3.3. Yield (%) of different products and time taken for the reaction of **1** & **4** with **7c** in xylene (0.42 M)

We repeated the reaction of (anthracen-9-yl)methyl sulfides (**1**-**6**) with electron deficient dienophiles **7a-c** at 0.042 M concentration in xylene. In this case we observed similar results and there was no change in the reaction pathway when the concentration of the substrates was changed. Hence the concentration of substrates has no effect on the reaction mechanism.

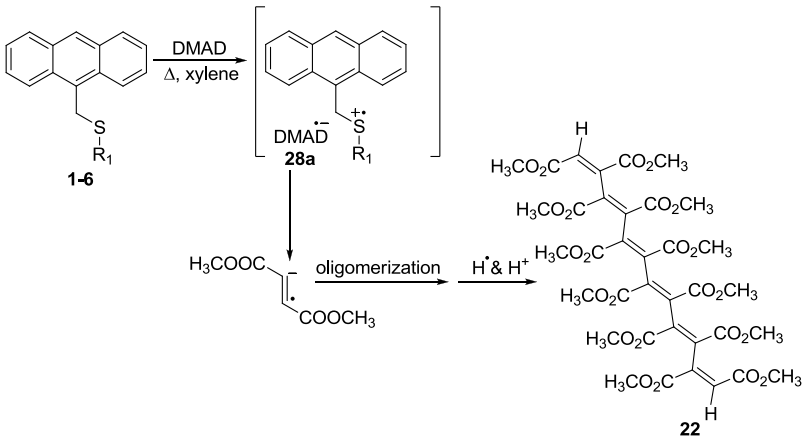
Similarities and subtle differences exist in the reaction of electron deficient dienophiles with anthracenemethanamines[14] and anthracenemethyl sulfides. Though similar products are generated in both the cases, mass balance is much better and reactions are cleaner in the case of sulfides. Irrespective of substrate concentration, Diels-Alder reaction predominates in the case of sulfides. It appears that sulfides are not as efficient as tertiary amines in single electron transfer reactions with electron deficient acetylenes. However, products arising through single electron transfer such as lepidopterene (**10**), 1,2-bis(9-anthracenyl)ethane (**9**) and 9-methylanthracene (**8**) are formed in negligible amounts and their presence was ascertained by GC-MS and/or LC-MS

analysis. As with amines, anthraquinone (**13**) is probably generated through the involvement of adventitious oxygen.[39-41] Mechanism for the generation of products **8**-**11** from anthracenemethyl methyl sulfide (**1**) is briefly indicated in Scheme 3.3. Products such as 9-methylanthracene (**8**), 1,2-bis(9-anthracenyl)ethane (**9**), lepidopterene (**10**), and 9-anthraldehyde (**11**) were formed from a common intermediate: sulfide radical cation[42] **23** generated through single electron transfer to **7a, 7b** or **7c** (*path **a***, Scheme 3.1). Degradation of **23** initiated by either hydrogen atom or proton loss may be understood in terms of pathways indicated in Scheme 3.3. Hydrogen atom loss from the methylene carbon leads to (anthracen-9-yl)(methylene)sulfonium ion precursor (**24**) of 9-anthraldehyde (**11**). On the other hand, proton loss from the methyl group followed by carbon-sulfur bond cleavage with loss of elements of thioformaldehyde leads to 9-anthracenemethyl radical (**26**). Homolytic cleavage of C-S bond in sulfides and aldehyde formation from organic sulfides has literature precedence.[43-46] Hydrogen atom abstraction by **26** leads to the formation of 9-methylanthracene (**8**). Isomers **9** and **10** are formed by dimerization of 9-anthracenemethyl radical[26,32,47] which in turn is a clear indicator to involvement of radical pathway in the reaction (Scheme 3.3). DMAD radical anion (**28a**) formed via single electron transfer mediated pathway (*path **a***, Scheme 3.1) undergoes oligomerization to form the DMAD hexamer **22** (Scheme 3.4) along with other unidentified oligomeric materials. Similarly, DBA radical anion (**28b**) formed via the single electron

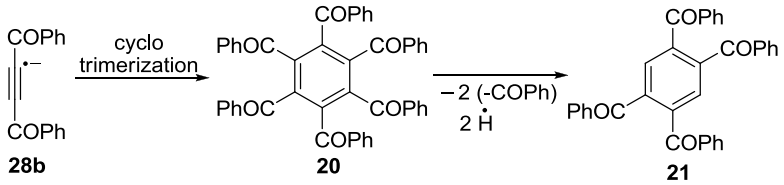
transfer mediated pathway (*path* **a**, Scheme 3.1) undergo cyclotrimerization to form hexabenzoylbenzene (**20**) which on further debenzoylation reaction followed by hydrogen atom abstraction forms tetrabenzoylbenzene (**21**) (Scheme 3.5).



Scheme 3.3



Scheme 3.4



Scheme 3.5

3.3.1.2. Reactions in polar aprotic solvents: Dimethylformamide and Acetonitrile

We explored the outcome of the reaction in non-nucleophilic polar solvents or polar aprotic solvents such as dimethylformamide (DMF) and acetonitrile. Though **1-6** exhibited appreciable solubility in acetonitrile, they were only sparingly soluble in DMF. At refluxing temperature, **1-6** exhibited moderate solubility (upto 0.42 M) in DMF. Hence, we could not explore

concentration dependent transformation of **1-6** with **7a-c** in DMF at lower temperatures. By selecting both DMF and acetonitrile, we could examine the effect of temperature as well as concentration on the reaction. We refluxed 0.42 M solution of (anthracen-9-yl)methyl sulfides **1-6** with 2 equivalents of **7a** in DMF. After completion of reaction different products were isolated. Products obtained were identical to those in the reactions in nonpolar medium, but in different yields. Diels-Alder adduct **(14-19)a** was the major product. Some amount of electron transfer mediated products and oxidation product were also formed. The yield (%) of different products obtained and the time taken for the reaction was depicted in the Table 3.4. As with the reactions in xylene, even at a substrate concentration of 0.042 M, product ratio remained unchanged.

Sulfide	**Reaction Time** (h)	**8** (%)	**9** (%)	**10** (%)	**11** (%)	**12** (%)	**13** (%)	**(14-19)a** (%)	**22** (%)
1	20	1	<1	<1	10	8	3	50	<1
2	16	<1	<1	<1	8	5	3	56	<1
3	20	<1	<1	<1	6	3	1	57	<1
4	14	<1	<1	<1	13	11	1	49	<1
5	16	<1	<1	<1	6	10	2	53	<1
6	16	1	<1	<1	3	7	2	58	<1

Table 3.4. Yield (%) of different products and time taken for the reaction of **1-6** with **7a** in DMF (0.42 M).

To assess the effect of nature and reactivity of dienophiles, we carried out the reaction of 0.42 M solution of **1-6** with 2 equivalents of DBA and DBE. These reactions also gave the same products as that of the products obtained in xylene reaction, but in different yields. Based on these results, we conclude that the reaction proceeded through the same mechanism in both nonpolar and polar aprotic solvents (Scheme 3.3). The yield (%) of different products obtained and the time taken for the reaction of **1-6** with **7b** in polar aprotic media, DMF can be obtained from the Table 3.5. Details of time taken and the yield (%) of products obtained by the reaction of **1** & **4** with **7c** in DMF are collected in Table 3.6.

Sulfide	**Reaction Time** (h)	**8** (%)	**9** (%)	**10** (%)	**11** (%)	**13** (%)	**(14-19)b** (%)	**20** (%)	**21** (%)
1	15	<1	<1	<1	10	2	56	<1	<1
2	10	1	<1	<1	5	5	76	<1	<1
3	14	<1	<1	<1	1	7	64	<1	<1
4	15	2	<1	<1	2	5	59	<1	<1
5	18	3	<1	<1	2	1	61	<1	<1
6	16	<1	<1	<1	10	3	63	<1	<1

Table 3.5. Yield (%) of different products and time taken for the reaction of **1-6** with **7b** in DMF (0.42 M).

Sulfide	Reaction Time (h)	8 (%)	9 (%)	10 (%)	11 (%)	13 (%)	14c/17c (%)	Unchanged 1/4 (%)
1	48	<1	<1	<1	6	<1	36	39
4	48	<1	<1	<1	4	<1	39	41

Table 3.6. Yield (%) of different products and time taken for the reaction of **1** & **4** with **7c** in DMF (0.42 M)

All products were completely characterized on the basis of spectral and analytical data, and where applicable by comparison with authentic samples prepared through reported procedures. Formation of 9-methylanthracene (**8**), for example, was confirmed by TLC and MS data. Similarly, formation of 9-anthraldehyde (**11**), 9,10-anthraquinone (**13**), 1,2-bis(9-anthracenyl)ethane (**9**) and lepidopterene (**10**) are confirmed by IR, ^{1}H NMR, ^{13}C NMR and MS data.

3.3.1.3. Reactions in polar protic medium: Alcohol, Methanol

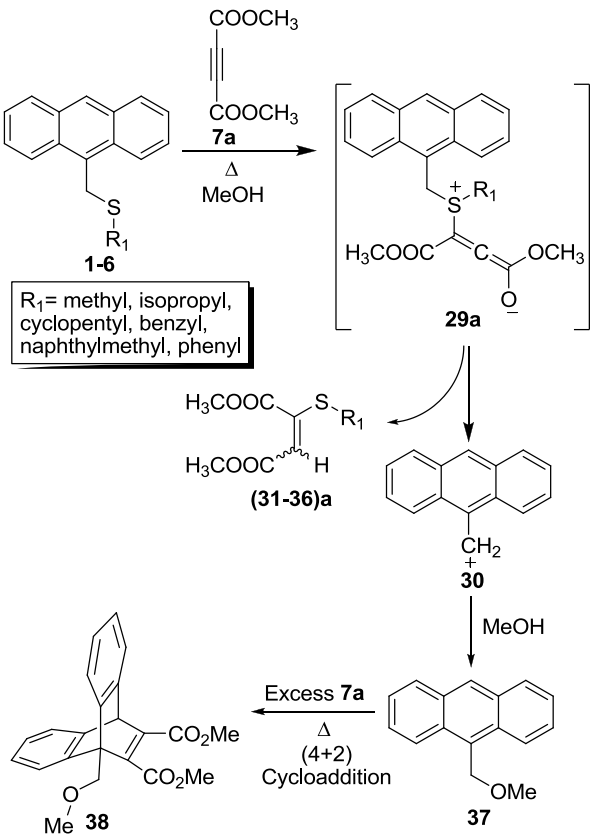
As stated earlier, we reasoned that reactions involving polar transition states (*path **b***) should be more competitive in polar protic solvents. With a view to test this hypothesis, we examined the reactions of **1-6** with dienophiles **7a**, **7b** and **7c** in polar protic solvents. We selected methanol (highly polar, but low boiling) and acetic acid (intermediate polarity and boiling point) for this investigation. Anthracenemethyl sulfides **1-6** exhibited only limited solubility in methanol. Hence reactions in methanol were

carried out at a lower concentration. A 0.17 M solution of (anthracen-9-yl)methyl sulfides **1-6** was refluxed with 2 equivalents of DMAD (**7a**) in methanol, we observed the formation of 9-(methoxymethyl)anthracene[48-51] (**37**) and thio substituted maleate/fumarate[52-54] **(31-36)a** in good yields along with products **8-10**, **12**, **13** and Diels-Alder adduct **(14-19)a** (Chart 3.2) in minor amounts. Diels-Alder adduct of 9-(methoxymethyl)anthracene[48,55] **38** was also obtained in low yields (Table 3.7, Scheme 3.6). Here we could not isolate **33a** in pure form. When (anthracen-9-yl)methyl naphthylmethyl sulfide (**5**) is taken as the substrate we could isolate dimethyl(2-naphthylmethylthio)maleate (**35a$_m$**) and dimethyl(2-naphthylmethylthio)fumarate (**35a$_f$**) in moderate yields. In the case of (anthracen-9-yl)methyl phenyl sulfide (**6**), the reaction is somewhat slow and about 30% of sulfide remained unchanged in the reaction. Yield (%) of different products obtained and time taken for the reaction is collected in Table 3.7.

Sulfide	Reaction Time (h)	8 (%)	9 (%)	10 (%)	12 (%)	13 (%)	(14-19)a (%)	(31-36)a (%)	37 (%)	38 (%)
1	8	<1	<1	3	8	2	<1	35	41	6
2	2	3	<1	6	12	3	<1	34	42	2
3	7	3	<1	2	7	11	<1	27	58	3
4	3	<1	<1	<1	7	7	<1	30	40	1
5	15	<1	<1	2	8	<1	<1	19- **35a$_m$** 21- **35a$_f$**	43	4
6	48	<1	<1	<1	4	<1	10	10	35	<1

Table 3.7. Yield (%) of different products and time taken for the reaction of **1-6** with **7a** in methanol (0.17 M).

We propose that nucleophilic attack of (anthracen-9-yl)methyl sulfides **1-6** on DMAD (**7a**) in a Michael type addition pathway generates Michael adduct/zwitterion[54,56,57] **29a** (Scheme 3.6). This leads to the weakening and eventual cleavage of C-S bond giving rise to 9-anthracenemethyl cation[31] (**30**) and **(31-36)a**. Cation **30** is captured by the solvent to give 9-(methoxymethyl)anthracene (**37)** that in turn undergoes (4+2) cycloaddition reaction with excess DMAD (**7a**) to form **38**.



Scheme 3.6

Minor products are formed through single electron transfer mediated pathways and oxidation reaction of (anthracen-9-yl)methyl sulfides (**1-6**) (Chart 3.2). In reactions done in alcohol solvents, when DMAD (**7a**) is taken as the electron deficient acetylene, we observed competition between one electron transfer (*path **a***), two electron transfer (*path **b***) and Diels-Alder reactions (*path **c***). From experimental results, we conclude that Michael type addition (*path **b***) is the major pathway.

To study the effect of dienophiles in methanol reaction, we repeated the reaction of **1-6** with **7b** and **7c**. A 0.11 M solution of **1-6** was refluxed with 2 equivalents of **7b** and **7c** in methanol, Diels-Alder adduct **(14-19)b** and **(14-19)c** were obtained in major amounts. In the case of reaction of (anthracen-9-yl)methyl phenyl sulfide (**6**) with **7b** about 60% of sulfide remained unchanged in the reaction due to its limited solubility in methanol. Single electron transfer mediated products **8-11** and oxidation product **13** were obtained in negligible amounts (Chart 3.2). Due to the lesser reactivity of DBE (**7c**) about 30-37% of sulfide remained unchanged in the reaction of **1-6** with **7c**. The yield (%) of different products obtained during the reaction between anthracenemethyl sulfides **1-6** and **7b** and time taken for the reaction are depicted in Table 3.8. Table 3.9 shows the yield (%) of products obtained by the reaction of **1** and **4** with **7c**.

Sulfide	Reaction Time (h)	8 (%)	9 (%)	10 (%)	11 (%)	13 (%)	(14-19)b (%)
1	30	<1	<1	<1	4	2	61
2	27	<1	<1	<1	3	2	67
3	24	<1	<1	<1	2	4	57
4	25	<1	<1	1	3	2	60
5	40	<1	<1	2	6	5	51
6	48	<1	<1	<1	12	6	20

Table 3.8. Yield (%) of different products and time taken for the reaction of **1-6** with **7b** in methanol (0.11 M).

Sulfide	Reaction Time (h)	8 (%)	9 (%)	10 (%)	11 (%)	13 (%)	14c/17c (%)	Unchanged 1/4 (%)
1	48	<1	<1	<1	<1	<1	50	30
4	48	<1	<1	<1	<1	<1	50	37

Table 3.9. Yield (%) of different products and time taken for the reaction of **1** & **4** with **7c** in methanol (0.11 M).

Close examination of product distribution in the reaction of **1-6** with **7b** and **7c** reveals that *path* **c** (Scheme 3.1) involving normal cycloaddition reaction was the major reaction pathway. Some amount of single electron transfer mediated products such as **8-11** and **13** were also formed as minor products. Mechanism for the formation of **8-11** was depicted in Scheme 3.3.

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

We refluxed a 0.42 M solution of **1-6** with 2 equivalents of DMAD (**7a**) in glacial acetic acid. After the completion of reaction, (anthracen-9-yl)methyl acetate[58-61] (**39**) and thio substituted maleate/fumarate **(31-36)a** were obtained in major yield along with single electron transfer mediated products **8-11**, oxidation product **13**, Diels-Alder adduct **(14-19)a** and Diels-Alder adduct of (anthracen-9-yl)methyl acetate[62] **40** in minor yields. Here also when (anthracen-9-yl)methyl naphthylmethyl sulfide (**5**) is taken as the substrate we could isolate dimethyl(2-naphthylmethylthio)maleate (**35a$_m$**) and dimethyl(2-naphthylmethylthio)fumarate (**35a$_f$**) in moderate yields (Scheme 3.7). For reactions carried out in acetic acid, yield (%) of different products obtained and the reaction time is depicted in the Table 3.10. Here the competition between one electron transfer (*path **a***), two electron transfer (Michael addition, *path **b***) and Diels-Alder reaction (*path **c***) occurs, the two electron transfer (*path **b***) is the major one. No change in product distribution was observed when the reaction was repeated at 0.042 M substrate concentration.

Sulfide	Reaction Time (h)	8 (%)	9 (%)	10 (%)	11 (%)	13 (%)	(14-19)a (%)	(31-36)a (%)	39 (%)	40 (%)
1	3	<1	<1	<1	6	<1	<1	18	63	4
2	7	<1	<1	1	13	<1	<1	18	49	5
3	2	<1	<1	3	11	<1	<1		59	4
4	3	<1	<1	3	<1	<1	<1	20	53	3
5	3	<1	<1	3	5	<1	<1	16- **35a$_m$** 18- **35a$_f$**	35	7
6	6	<1	3	8	15	<1	4	15	47	9

Table 3.10. Yield (%) of different products and time taken for the reaction of **1-6** with **7a** in glacial acetic acid (0.42 M).

As in the previous cases, in order to study the effect of dienophiles in acetic acid reaction, we repeated the reaction of **1-6** with **7b** and **7c**. A 0.42 M solution of **1-6** was refluxed with **7b**, Diels-Alder adduct **(14-19)b** were obtained in major yields along with (anthracen-9-yl)methyl acetate (**39**) and thiosubstituted dibenzoylethylene[63-66] **(31-35)b** in moderate yields. In the case of the reaction of (anthracen-9-yl)methyl phenyl sulfide (**6**) with **7b** no products corresponding to Michael type addition pathway (*path **b***) were observed. Products **8-11,** hexabenzoylbenzene (**20**) and tetrabenzoylbenzene (**21**) were obtained in minor yields. There occurs a competition between single electron transfer (*path **a***), two electron transfer (*path **b***) and Diels-Alder reactions (*path **c***) in the reaction of **1-6** with **7b**. But Diels-Alder reaction (*path* **c**) was the major reaction pathway. Mechanisms for the formation of minor

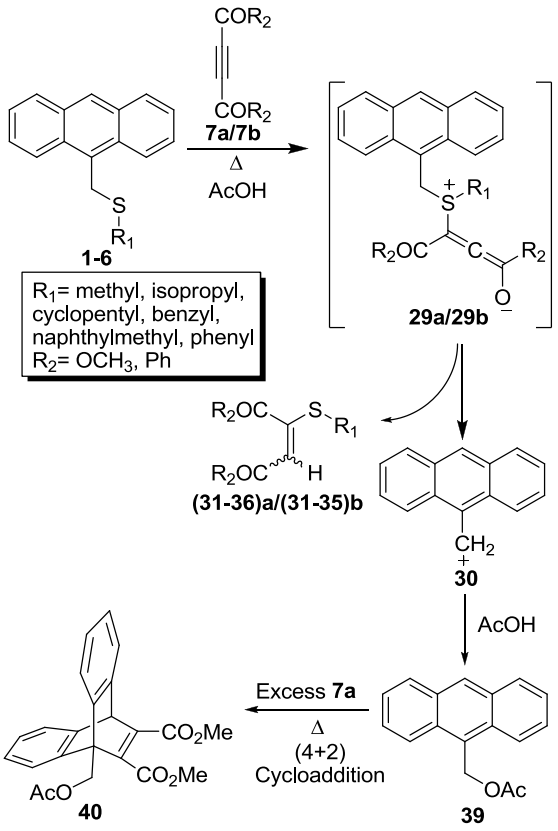
products are shown in schemes 3.3 and 3.5. Yield (%) of different products obtained and the reaction time is depicted in the Table 3.11. For studying the concentration dependency we carried out the reaction of **1-6** at 0.042 M concentration with **7b**. But similar results were obtained as that of concentrated reaction. Hence there is no concentration dependency in the reaction.

Sulfide	Reaction Time (h)	8 (%)	9 (%)	10 (%)	11 (%)	13 (%)	(14-19)b (%)	20 (%)	21 (%)	(31-35)b (%)	39 (%)
1	13	<1	<1	6	19	<1	23	2	<1	10	29
2	11	<1	<1	4	10	<1	27	3	<1	10	30
3	10	<1	<1	5	5	<1	24	3	<1	12	37
4	9	<1	<1	3	13	<1	22	2	<1	9	13
5	3	<1	<1	4	4	<1	34	6	<1	12	23
6	6	<1	<1	2	21	<1	65	4	1	-	-

Table 3.11. Yield (%) of different products and time taken for the reaction of **1-6** with **7b** in glacial acetic acid (0.42 M).

Generation of solvolysis product **39** suggests mechanism similar to that observed in methanol. The nucleophilic attack of (anthracen-9-yl)methyl sulfides **1-6** on acetylene **7a** or **7b** in a Michael type addition pathway (*path **b***) generates Michael adduct/zwitterion **29a/b** (Scheme 3.7). This leads to the weakening and eventual cleavage of C-S bond giving rise to 9-anthracenemethyl cation (**30**) and **(31-36)a/(31-35)b**. Cation **30** is

captured by the solvent, glacial acetic acid to give (anthracen-9-yl)methyl acetate **39**. Compound **39** undergo (4+2) cycloaddition reaction with excess **7a** to give **40**.



Scheme 3.8

In continuation of the study on the effect of dienophiles, we repeated the reaction of **1** & **4** with **7c** in glacial acetic acid at 0.42 M substrate concentration. In this case, Diels-Alder reaction (*path **c***) predominates over single electron transfer reaction (*path **a***).

Mechanism for the formation of minor products such as **8-11** and **13** are shown in scheme 3.3. The yield (%) of different products formed by the reaction of **1** & **4** with **7c** are depicted in Table 3.12. Due to lesser reactivity of DBE (**7c**), the reaction was slow and about 40% of sulfides remained unchanged even after 48h.

Sulfide	Reaction Time (h)	8 (%)	9 (%)	10 (%)	11 (%)	13 (%)	14c/17c (%)	Unchanged 1/4 (%)
1	48	<1	<1	<1	2	<1	37	40
4	48	<1	<1	<1	1	<1	50	40

Table 3.12. Yield (%) of different products and time taken for the reaction of **1** & **4** with **7c** in glacial acetic acid (0.42 M).

3.4. Conclusion

We have illustrated interesting solvent dependent reactions of (anthracen-9-yl)methyl sulfides with electron deficient acetylenes and explored the mechanistic pathways of these reactions under different conditions. Depending on the nature of solvent and substituents on dienophile the mechanism of the reaction changes from *path **a*** to *path **c*** that is from single electron transfer reaction to Diels-Alder reaction. We performed the reaction in solvents such as xylene, acetonitrile, DMF, methanol and acetic acid at low and high concentrations. For studying the effect of dienophiles, we have done the reaction using DMAD, DBA and DBE.

In nonpolar and polar aprotic media, there exists a competition between single electron transfer and Diels-Alder reactions, but Diels-Alder reaction was the major pathway. Single electron transfer mediated products such as 9-methylanthracene, 1,2-bis(9-anthracenyl)ethane, lepidopterene, 9-anthraldehyde, dimethyl 1-oxo-1*H*-benzo[*de*]anthracene-2,3-dicarboxylate, DMAD hexamer, hexabenzoylbenzene and tetrabenzoylbenzene and oxidation product anthraquinone were obtained as minor products.

In polar protic solvents, when DMAD was used as the reactive acetylene, there exists a competition between single electron transfer, two electron transfer and Diels-Alder reactions. Here two electron transfer reaction is the major pathway. When DBA was used as the acetylene, Diels-Alder reaction takes precedence over both Michael addition and single electron transfer reactions.

Rate of the reaction is directly proportional to the magnitude of electron deficiency of the dienophile. Hence we have repeated the reaction using DBE as dienophile. DBE has less reactivity than DMAD and DBA. So the reaction of (anthracen-9-yl)methyl sulfides with DBE is very slow in comparison with DBA and DMAD reactions. Also an appreciable amount of substrates remained unchanged in the reaction. Here also Diels-Alder reaction is the major reaction pathway and some amount of single electron transfer mediated products and oxidation product are obtained as minor products.

We have demonstrated the generality of the observed transformations using a variety of anthracenemethyl sulfides. Our results clearly indicate that the course of the reactions is not significantly altered with change in substituents on the different sulfides.

3.5. Experimental

3.5.1. General Techniques

All reactions were carried out in oven dried glass wares. 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. All the reactions and chromatographic separations were monitored by thin layer chromatography (TLC). Aluminium sheets coated with silica gel (*Merck*) were used for thin layer chromatography. Separation and purification of compounds were done by column chromatography using silica gel (*Spectrochem Chemicals*, 60-120 mesh). The products were further purified by recrystallization from suitable solvent systems. 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. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz on a *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 electrospray ionization (ESI) method using GC-MS (*Agilent GC-7890A, Mass-5975C*) and fast atom bombardment (FAB) using *JMS 600 JEOL* mass spectrometers. All new compounds were identified on the basis of spectral and analytical data. Relevant references are cited for known compounds.

3.5.2. Dibenzoylacetylene

Dibenzoylacetylene[67] (**7b**) was prepared by a known procedure (75%, mp 109-110 °C).

3.5.3. Dibenzoylethylene

Dibenzoylethylene[68] (**7c**) was synthesized by a known procedure (70%, mp 110-111 °C).

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

3.5.4.1. Reactions in nonpolar solvent-xylene.

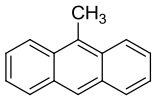
3.5.4.1.1. General experimental procedure for the reaction of (anthracen-9-yl)methyl sulfide (1-6) with DMAD (7a).

To a solution (0.42 M) of (anthracen-9-yl)methyl sulfide (**1-6**) in xylene, DMAD (**7a**, 2 equivalents) was added and the mixture was refluxed. Progress of the reaction was monitored by TLC. After the reaction has completed, the reaction mixture was cooled and the solvent was removed under reduced pressure. The residue obtained was separated and purified by column chromatography on silica gel. Elution with hexane gave **8**, and **9** was obtained by the elution using a mixture (9:1) of hexane and dichloromethane. Further elution with a mixture (4:1) of hexane and dichloromethane yielded **10**. **11** and **13** were obtained by elution with a mixture of (7:3) hexane and dichloromethane. **12** was obtained by elution with a mixture (3:2) of hexane and dichloromethane. **(14-19)a** was obtained by elution with a mixture of (2:3) hexane and dichloromethane. Finally **22** was obtained by elution with (1:4) hexane-dichloromethane mixture. Some amount of polymerized material is also formed in the reaction.

In a repeat run, a 0.042 M solution of **1-6** in xylene was refluxed with DMAD (**7a**, 2 equivalents). Solvent was removed under reduced pressure and the residue was purified by column

chromatography on silica gel. Product distribution was similar to that obtained in the reaction carried out at 0.42M.

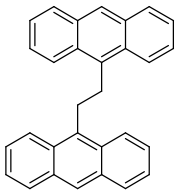
Compound 8:[25]



mp: 78-81 °C.

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

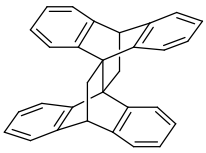
Compound 9:[29]



mp: 238-239 °C.

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

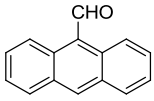
Compound 10:[31]



mp: 316-318 °C.

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

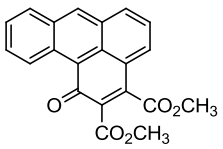
Compound 11:[35]



mp: 103-105 °C.

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

Compound 12:



Yellow puffy solid.

mp: 166 °C.

IR ν_{max} (KBr): 3016, 2955, 2925, 2853, 1732, 1713, 1665, 1437, 1273, 768 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 8.87-7.52 (m, 8H), 4.05 (s, 3H), 3.98 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 182.08, 167.71, 164.69, 134.77, 133.87, 132.79, 132.16, 130.91, 130.06, 128.37, 128.22, 127.61, 127.53, 127.25, 127.22, 126.20, 124.70, 122.60, 122.08, 52.15, 52.04.

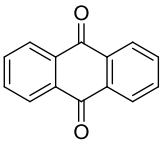
MS: *m/z* 347 $(M+1)^+$.

Elemental analysis calculated for

$C_{21}H_{14}O_5$: C, 72.83; H, 4.07.

Found: C, 72.75; H, 3.98.

Compound 13:[36]



mp: 284-286 °C.

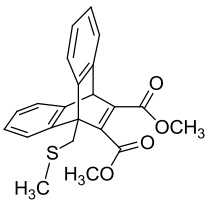
MS: *m/z* 208 (M^+), 180 (*M-28*).

Compound 14a:

White crystalline solid.

mp: 172 °C.

IR ν_{max} (KBr): 3066, 2968, 2947, 2912, 1728, 1715, 1628, 1433, 1328, 1264, 754 cm^{-1}.



^{1}H NMR ($CDCl_3$): δ 7.52-6.99 (m, 8H), 5.56 (s, 1H), 3.95 (s, 2H), 3.76 (s, 3H), 3.75 (s, 3H), 2.35 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 167.36, 164.17, 152.06, 145.76, 143.83, 143.05, 125.19, 125.13, 123.54, 122.37, 72.71, 64.21, 56.05, 52.30, 51.46, 50.73, 21.93.

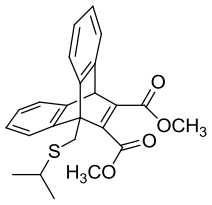
MS: *m/z* 380 (M^+).

Elemental analysis calculated for

$C_{22}H_{20}O_4S$: C, 69.45; H, 5.30; S, 8.43.

Found: C, 69.36; H, 5.25; S, 8.38.

Compound 15a:



White crystalline solid.

mp: 130 °C.

IR ν_{max} (KBr): 3024, 2998, 2957, 2915, 2858, 1712, 1697, 1592, 1380, 1328, 1297, 618 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.54-6.98 (m, 8H), 5.55 (s, 1H), 3.96 (s, 2H), 3.75 (s, 3H), 3.74 (s, 3H), 3.15-3.05 (m, 1H), 1.42 (d, 6H, *J*=6.4 Hz).

^{13}C NMR ($CDCl_3$): δ 167.43, 164.32, 145.67, 144.60, 143.99, 125.38, 125.05, 123.61, 122.49, 56.89, 52.34, 51.97, 51.05, 38.39, 29.99, 23.46.

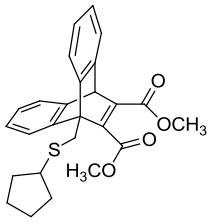
MS: *m/z* 408 (M^+).

Elemental analysis calculated for

$C_{24}H_{24}O_4S$: C, 70.56; H, 5.92; S, 7.85.

Found: C, 70.43; H, 5.47; S, 7.74.

Compound 16a:



White crystalline solid.

mp: 176 °C.

IR ν_{max} (KBr): 3066, 3009, 2946, 2869, 1712, 1623, 1598, 1431, 1328, 1276, 1209, 1074, 768, 618 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.54-6.98 (m, 8H), 5.55 (s, 1H), 3.96 (s, 2H), 3.75 (s, 3H), 3.74 (s, 3H), 3.31-3.26 (m, 1H), 2.16-1.72 (m, 8H).

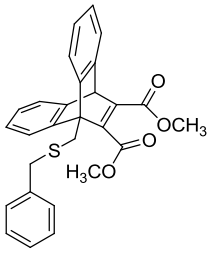
^{13}C NMR ($CDCl_3$): δ 167.46, 164.29, 145.66, 143.79, 125.36, 125.03, 123.60, 122.49, 56.98, 52.33, 52.02, 50.98, 47.14, 33.72, 30.82, 24.85.

MS: *m/z* 434 (M^+).

Elemental analysis calculated for

$C_{26}H_{26}O_4S$: C, 71.86; H, 6.03; S, 7.38.
Found: C, 71.76; H, 5.96; S, 7.32.

Compound 17a:



White crystalline solid.

mp: 162°C.

IR ν_{max} (KBr): 3058, 3023, 2938, 2839, 1717, 1619, 1598, 1447, 1425, 1332, 1280, 1210, 774, 705 cm^{-1}.

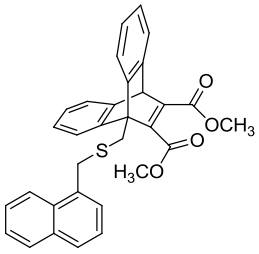
^{1}H NMR ($CDCl_3$): δ 7.49-6.98 (m, 13H), 5.54 (s, 1H), 3.94 (s, 2H), 3.86 (s, 2H), 3.76 (s, 3H), 3.75 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 167.42, 164.27, 145.53, 144.04, 137.99, 129.01, 128.69, 127.29, 125.39, 125.02, 123.64, 122.43, 56.75, 52.38, 52.17, 50.96, 39.38, 30.98.

MS: *m/z* 456 (M^+).

Elemental analysis calculated for
$C_{28}H_{24}O_4S$: C, 73.66; H, 5.30; S, 7.02.
Found: C, 73.58; H, 5.23; S, 6.94.

Compound 18a:



White crystalline solid.

mp: 164°C.

IR ν_{max} (KBr): 3061, 3035, 2946, 2843, 1727, 1707, 1618, 1598, 1457, 1427, 1333, 1281, 1213, 779, 705 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 8.31-6.89 (m, 15H), 5.52 (s, 1H), 4.39 (s, 2H), 3.89 (s, 2H), 3.74 (s, 3H), 3.69 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 162.15, 159.02, 140.24, 138.83, 128.95, 128.10, 126.32, 123.62, 123.19, 122.15, 120.99, 120.73, 120.09, 119.96, 119.73, 118.91, 118.31, 117.24, 51.40, 47.10, 46.90, 45.71, 31.67, 25.91.

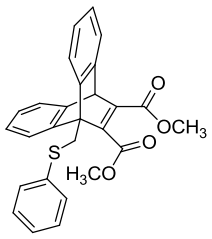
MS: *m/z* 506 (M^+).

Elemental analysis calculated for

$C_{32}H_{26}O_4S$: C, 75.87; H, 5.17; S, 6.33.

Found: C, 75.79; H, 5.10; S, 6.27.

Compound 19a:



White crystalline solid.

mp: 138°C.

IR ν_{max} (KBr): 3038, 3019, 2993, 2941, 2832, 1732, 1712, 1623, 1588, 1479, 1431, 1328, 1266, 1209, 1115, 1069, 731 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.60-7.01 (m, 13H), 5.59 (s, 1H), 4.40 (s, 2H), 3.76 (s, 3H), 3.66 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 167.07, 164.16, 145.54, 144.04, 137.01, 129.53, 129.20, 126.61, 125.54, 125.09, 123.76, 56.25, 52.41, 52.27, 50.98, 33.42.

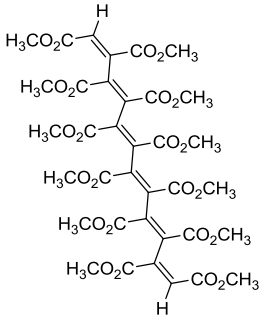
MS: *m/z* 442 (M^+).

Elemental analysis calculated for

$C_{27}H_{22}O_4S$: C, 73.28; H, 5.01; S, 7.25.

Found: C, 73.18; H, 4.92; S, 7.16.

Compound 22:



Off-white crystalline solid.

mp: 116 °C.

IR ν_{max} (KBr): 2956, 1753, 1727, 1253 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 8.65 (2H, s), 3.96 & 3.94 (two singlets, 30H), 3.89 (s, 6H).

MS: *m/z* 854 *(M^+).*

Elemental analysis calculated for

$C_{36}H_{38}O_{24}$: C, 50.59; H, 4.48.

Found: C, 50.38; H, 4.36.

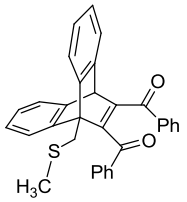
3.5.4.1.2. General experimental procedure for the reaction of (anthracen-9-yl)methyl sulfides (1-6) with DBA (7b).

To a solution (0.42 M) of (anthracen-9-yl)methyl sulfide (**1-6**) in xylene, DBA (**7b**, 2 equivalents) was added and the mixture was refluxed. Progress of the reaction was monitored by TLC. After the reaction has completed, the reaction mixture was cooled and the solvent was removed under reduced pressure. Products obtained were separated and purified by column chromatography on silica gel. Elution with hexane gave **8**, and **9** was obtained by the elution using a mixture (9:1) of hexane and dichloromethane. Further elution with a mixture (4:1) of hexane and dichloromethane yielded **10**. **11** and **13** were obtained by elution with a mixture of (7:3) hexane and dichloromethane. (**14-19**)**b** was obtained by elution with a mixture of (2:3) hexane and dichloromethane. A small amount of **20** and **21** were obtained by elution with (1:9) and

(1:4) hexane-dichloromethane mixture respectively. Some amount of polymerized material is also formed in the reaction.

In a repeat run, a 0.042 M solution of **1-6** in xylene was refluxed with DBA (**7b**, 2 equivalents). Solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel. Product distribution was similar to that obtained in the reaction carried out at 0.42M.

Compound 14b:



Off-white crystalline solid.
mp: 178 °C.

IR ν_{max} (KBr): 3061, 3029, 2983, 2911, 2853, 1660, 1645, 1598, 1448, 1385, 1276, 1069, 690 cm^{-1}.

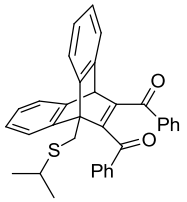
^{1}H NMR ($CDCl_3$): δ 7.55-7.02 (m, 18H), 5.47 (s, 1H), 4.02 (s, 2H), 1.95 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 194.50, 193.69, 151.88, 145.86, 138.28, 137.23, 132.89, 132.35, 128.95, 128.12, 127.81, 125.44, 125.21, 123.61, 53.44, 33.22, 18.09.

MS: *m/z* 473 $(M+1)^+$, 105.

Elemental analysis calculated for
$C_{32}H_{24}O_2S$: C, 81.33; H, 5.12; S, 6.78.
Found: C, 81.23; H, 5.06; S, 6.71.

Compound 15b:



Off-White crystalline solid.

mp: 150°C.

IR ν_{max} (KBr): 3061, 3035, 2952, 2911, 2863, 1660, 1600, 1592, 1453, 1396, 1318, 1256, 1240, 705, 612 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.48-6.94 (m, 18H), 5.39 (s, 1H), 3.93 (s, 2H), 2.55-2.49 (m, 1H), 1.12-0.86 (br, 6H).

^{13}C NMR ($CDCl_3$): δ 194.44, 193.87, 151.39, 145.93,

138.24, 137.24, 132.89, 132.31, 129.02, 128.12, 127.73, 125.41, 125.20, 123.58, 60.61, 53.37, 38.94, 29.87.

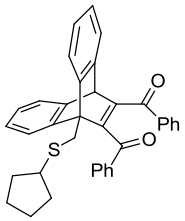
MS: *m/z* 500 (M^+), 105.

Elemental analysis calculated for

$C_{34}H_{28}O_2S$: C, 81.57; H, 5.64; S, 6.40.

Found: C, 81.49; H, 5.52; S, 6.35.

Compound 16b:



Off-White crystalline solid.

mp: 182°C.

IR ν_{max} (KBr): 3061, 3035, 2946, 2905, 2869, 1660, 1608, 1588, 1448, 1396, 1261, 1110, 705, 685, 602 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.56-7.01 (m, 18H), 5.46 (s, 1H), 4.02 (s, 2H), 2.86-2.79 (m, 1H), 1.59-1.46 (m, 8H).

^{13}C NMR ($CDCl_3$): δ 194.47, 193.87, 151.35, 145.92, 138.25, 137.25, 132.87, 132.28, 129.03, 128.11, 127.71, 125.39, 125.18, 123.57, 60.56, 53.36, 47.45, 30.55, 24.58.

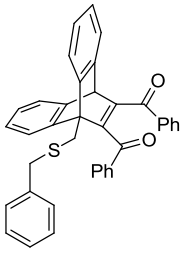
MS: *m/z* 526 (M^+), 105.

Elemental analysis calculated for

$C_{36}H_{30}O_2S$: C, 82.10; H, 5.74; S, 6.09.

Found: C, 81.99; H, 5.69; S, 6.02..

Compound 17b:



Off-White crystalline solid.

mp: 170°C.

IR ν_{max} (KBr): 3066, 3029, 2983, 2920, 2837, 1640, 1592, 1572, 1448, 1318, 1276, 1069, 690, 596 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.39-6.89 (m, 23H), 5.39 (s, 1H), 3.93 (s, 2H), 3.46 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 194.53, 194.03, 151.92, 145.82, 138.39, 137.53, 137.29, 132.94, 132.46, 128.98, 128.39, 128.17, 127.91, 126.98, 125.46, 125.23, 123.61, 60.49, 53.44, 39.33, 30.64.

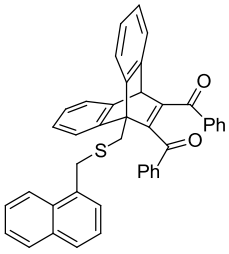
MS: *m/z* 548 (M^+), 105.

Elemental analysis calculated for

$C_{38}H_{28}O_2S$: C, 83.18; H, 5.14; S, 5.84.

Found: C, 83.09; H, 5.08; S, 5.78.

Compound 18b:



Off-White crystalline solid.

mp: 166°C.

IR ν_{max} (KBr): 3061, 2972, 2926, 2858, 1644, 1590, 1540, 1448, 1396, 1266, 779, 690 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.83-7.05 (m, 25H), 5.46 (s, 1H), 4.08 (s, 2H), 3.99 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 194.55, 194.21, 152.21, 145.78, 138.51, 137.29, 133.90, 133.35, 132.95, 132.50, 131.50, 128.95, 128.18, 128.09, 127.96, 127.44, 125.98, 125.68, 125.44, 125.23, 123.94, 123.59, 60.32, 53.50, 53.40, 37.02, 30.98.

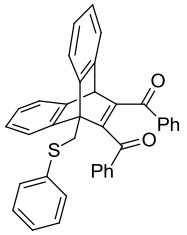
MS: *m/z* 598 (M^+).

Elemental analysis calculated for

$C_{42}H_{30}O_2S$: C, 84.25; H, 5.05; S, 5.36.

Found: C, 84.18; H, 4.97; S, 5.29.

Compound 19b:



Off-White crystalline solid.

mp: 140°C.

IR ν_{max} (KBr): 3061, 2978, 2920, 2848, 1655, 1592, 1448, 1396, 1322, 1261, 1074, 742, 690, 596 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.66-7.02 (m, 23H), 5.49 (s, 1H),

4.54 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 194.54, 193.85, 152.02, 145.74, 138.04, 137.17, 136.86, 132.93, 132.58, 129.58, 129.12, 128.98, 128.85, 128.14, 127.85, 126.66, 125.57, 125.26, 123.73, 58.90, 53.48, 33.81.

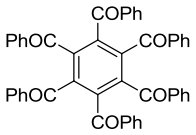
MS: *m/z* 534 (M^+).

Elemental analysis calculated for

$C_{37}H_{26}O_2S$: C, 83.12; H, 4.90; S, 6.00.

Found: C, 83.04; H, 4.83; S, 5.89.

Compound 20:



White crystalline solid.

mp: 284°C.

IR ν_{max} (KBr): 3057, 2922, 1667, 1595, 1449, 1229, 729 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.44-7.16 (m, 30H).

^{13}C NMR ($CDCl_3$): δ 195.06, 141.26, 136.51, 133.80, 129.83, 128.16.

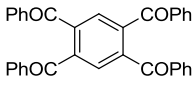
MS: *m/z* 702 (M^+).

Elemental analysis calculated for

$C_{48}H_{30}O_6$: C, 82.04; H, 4.30.

Found: C, 81.91; H, 4.19.

Compound 21:



Yellow solid.

mp: 232 °C.

IR ν_{max} (KBr): 3056, 2926, 1682, 1663, 1599, 1447, 1245, 694 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.83 (s, 2H), 7.77-7.39 (m, 20H).

^{13}C NMR ($CDCl_3$): δ 195.05, 141.51, 136.28, 133.72, 130.20, 129.93, 128.64.

MS: *m/z* 494 (M^+).

Elemental analysis calculated for

$C_{34}H_{22}O_4$: C, 82.58; H, 4.48.

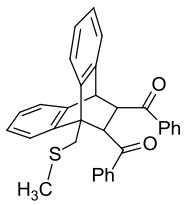
Found: C, 82.45; H, 4.39.

3.5.4.1.3. General experimental procedure for the reaction of (anthracen-9-yl)methyl sulfide (1 & 4) with DBE (7c).

To a solution (0.42 M) of **1** & **4** in xylene, DBE (**7c**, 2 equivalents) was added and the mixture was refluxed for 48h. 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 **8**, and **9** was obtained by the elution using a mixture (9:1) of hexane and dichloromethane. **10** was obtained by elution with a mixture of (4:1) hexane and dichloromethane followed by **11** and **13** were obtained by elution with (7:3) mixture of hexane and dichloromethane. Further elution with a mixture (2:3) of hexane and dichloromethane gave **14c/17c**. In this case, 42-45% of **1** & **4** remained unchanged in the reaction.

Compound 14c:

Off-white crystalline solid.
mp: 176 °C.



IR ν_{max} (KBr): 3061, 3029, 2983, 2911, 2853, 1660, 1645, 1598, 1448, 1385, 1276, 1069, 690 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.88-6.92 (m, 18H), 4.89 (d, 1H, *J*= 6 Hz), 4.45 (d, 1H, *J*= 1.6 Hz), 3.84 (dd, 1H, *J*= 6.4 Hz and 2 Hz), 3.7 (s, 2H), 3.67 (s, 2H), 2.03 (s,

3H).

^{13}C NMR ($CDCl_3$): δ 201.66, 197.27, 142.35, 139.65, 136.25, 133.18, 133.05, 128.85, 128.44, 128.28, 126.40, 126.27, 126.00, 125.85, 124.76, 122.78, 122.61, 54.20, 48.79, 36.13, 18.00.

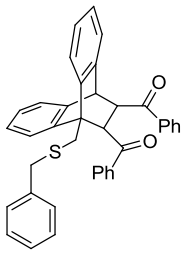
MS: *m/z* 475 $(M+1)^+$.

Elemental analysis calculated for

$C_{32}H_{26}O_2S$: C, 80.98; H, 5.52; S, 6.76.

Found: C, 80.91; H, 5.43; S, 6.69.

Compound 17c:



Off-White crystalline solid.

mp: 168 °C.

IR ν_{max} (KBr): 3074, 3031, 2935, 2848, 1684, 1600, 1442, 1388, 1226, 1060, 752 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.89-6.89 (m, 23H), 4.85 (d, 1H, *J*= 5.2 Hz), 4.43 (d, 1H, *J*=2 Hz), 3.85 (dd, 1H, *J*= 6 Hz and 2 Hz), 3.63 (s, 2H), 3.58 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 201.42, 197.30, 142.36, 139.55, 137.83, 136.26, 133.18, 133.07, 128.94, 128.86, 128.52, 128.31, 127.05, 126.35, 126.23, 125.98, 125.87, 124.69, 122.72, 54.27, 49.86, 48.78, 38.80, 33.26.

MS: *m/z* 551 $(M+1)^+$.

Elemental analysis calculated for

$C_{38}H_{30}O_2S$: C, 82.88; H, 5.49; S, 5.82.

Found: C, 82.79; H, 5.43; S, 5.76.

3.5.4.2. Reactions in polar aprotic media – DMF and Acetonitrile

Reactions in polar aprotic media follow the same procedure as that of 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 sulfide to give polar, intractable mixture. The products isolated in pure form are reported hereunder.

3.5.4.2.1. General experimental procedure for the reaction of (anthracen-9-yl)methyl sulfide (1-6) with DMAD (7a) in DMF.

In refluxing DMF, a 0.42 M solution of **1-6** on treatment with 2 equivalents of **7a** gave a mixture of **8**, **9**, **10**, **11**, **12**, **13**, **(14-19)a** and **22**.

In a repeat run, a 0.042 M solution of **1-6** with 2 equivalents of **7a** gave a mixture of **8**, **9**, **10**, **11**, **12**, **13**, **(14-19)a** and **22**.

3.5.4.2.2. General experimental procedure for the reaction of (anthracen-9-yl)methyl sulfide (1-6) with DBA (7b) in DMF.

In refluxing DMF, a 0.42 M solution of **1-6** on treatment with 2 equivalents of **7b** gave a mixture of **8**, **9**, **10**, **11**, **13**, **(14-17)b**, **20** and **21**.

In a repeat run, a 0.042 M solution of **1-6** with 2 equivalents of **7a** gave a mixture of **8**, **9**, **10**, **11**, **13**, **(14-19)b**, **20** and **21**.

3.5.4.2.3. General experimental procedure for the reaction of (anthracen-9-yl)methyl sulfide (1 & 4) with DBE (7c) in DMF.

In refluxing DMF, a 0.42 M solution of **1** & **4** on treatment with 2 equivalents of **7c** for 48h gave a mixture of **8**, **9**, **10**, **11**, **13**, **14c/17c** and about 39-41% of sulfide **1** & **4** remained unchanged in the reaction.

3.5.4.2.4. General experimental procedure for the reaction of (anthracen-9-yl)methyl sulfide (1-6) with (7a/7b/7c) in acetonitrile.

We have repeated the reactions of various anthracenemethyl sulfides in polar aprotic solvent-acetonitrile under similar conditions. A 0.42 M solution of **1-6** in acetonitrile was refluxed with 2 equivalents of **7a/7b/7c**. Progress of the reaction was monitored by TLC. The product mixture obtained was separated and purified by column chromatography on silica gel using hexane and dichloromethane.

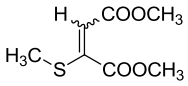
3.5.4.3. Reactions in polar protic medium – Alcohol, Methanol

(Anthracen-9-yl)methyl sulfides **1-6** have limited solubility in methanol and hence all the reactions were carried out at low concentration.

3.5.4.3.1. General experimental procedure for the reaction of (anthracen-9-yl)methyl sulfide (1-6) with DMAD (7a).

Treating a 0.17 M solution of **1-6** in methanol with DMAD (**7a**, 2 equivalents) and the mixture was refluxed. Progress of the reaction was monitored by TLC. After the reaction has completed, the reaction mixture was cooled and the solvent was removed under reduced pressure. The product mixture obtained was separated and purified by column chromatography on silica gel. Elution with hexane and a mixture (9:1) of hexane and dichloromethane gave **8** and **9** respectively. Elution using a mixture (4:1) of hexane and dichloromethane yielded **10**. **13** and **37** are obtained by elution with (7:3) hexane-dichloromethane mixture. Elution with (3:2) mixture of hexane and dichloromethane yielded **12**. Further elution with a mixture (2:3) of hexane and dichloromethane gave **(14-19)a** and (**31-36)a**. In the case of (anthracen-9-yl)methyl naphthylmethyl sulfide (**5**), $\mathbf{35a_m}$ (19%) & $\mathbf{35a_f}$ (21%) were isolated. Elution with a mixture (1:4) of hexane and dichloromethane gave **38**.

Compound 31a:



Yellow waxy material.

IR ν_{max} (KBr): 3005, 2952, 2926, 2854, 1737, 1715, 1591, 1437, 1259, 1202, 1167 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 6.28 (s, 1H), 3.86 (s, 3H), 3.76 (s, 3H), 2.34 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 164.93, 163.05, 150.39, 110.83, 52.12, 50.80, 13.62.

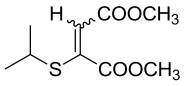
MS: *m/z* 190 (M^+).

Elemental analysis calculated for

$C_7H_{10}O_4S$: C, 44.20; H, 5.30; S, 16.86.

Found: C, 44.13; H, 5.22; S, 16.78.

Compound 32a:



Yellow waxy material.

IR ν_{max} (KBr): 3002, 2972, 2952, 2931, 2863, 1732, 1712, 1588, 1401, 1380, 1250, 1110 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 5.79 (s, 1H), 3.88 (s, 3H), 3.71 (s, 3H), 3.38-3.28 (m, 1H), 1.38-1.36 (d, 6H).

^{13}C NMR ($CDCl_3$): δ 165.12, 163.14, 148.83, 112.92, 52.02, 50.78, 35.77, 21.69.

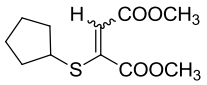
MS: *m/z* 218 (M^+).

Elemental analysis calculated for

$C_9H_{14}O_4S$: C, 49.52; H, 6.47; S, 14.69.

Found: C, 49.45; H, 6.41; S, 14.63.

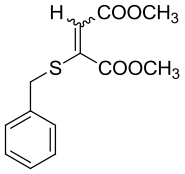
Compound 33a:



Yellow waxy material.

MS: *m/z* 244 (M^+).

Compound 34a: Yellow waxy material.



IR ν_{max} (KBr): 3020, 2967, 2858, 1726, 1589, 1431, 1392, 1261, 1205, 1105, 773 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.40-7.24 (m, 5H), 5.91 (s, 1H), 3.93 (s, 2H), 3.89 (s, 3H), 3.71 (s, 3H).

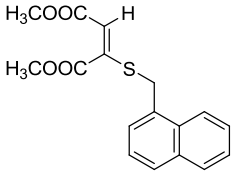
^{13}C NMR ($CDCl_3$): δ 165.74, 164.05, 149.82, 134.19, 128.95, 128.87, 128.03, 113.44, 53.10, 51.85, 36.57.

MS: *m/z* 266 (M^+).

Elemental analysis calculated for

$C_{13}H_{14}O_4S$: C, 58.63; H, 5.30; S, 12.04.
Found: C, 58.56; H, 5.24; S, 11.97.

Compound 35a$_m$: Yellow waxy material.



IR ν_{max} (KBr): 3009, 2957, 2853, 1732, 1592, 1431, 1384, 1266, 1209, 1110, 783 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 8.03-7.39 (m, 7H), 5.88 (s, 1H), 4.84 (s, 2H), 3.89 (s, 3H), 3.73 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 165.78, 164.12, 150.17, 133.95, 131.48, 129.47, 129.23, 128.97, 128.04, 126.77, 126.17, 125.42, 123.36, 113.58, 53.15, 51.89, 34.49.

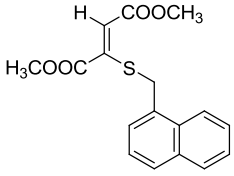
MS: *m/z* 316 (M^+).

Elemental analysis calculated for

$C_{17}H_{16}O_4S$: C, 64.54; H, 5.10; S, 10.14.

Found: C, 64.42; H, 5.02; S, 10.08.

Compound 35a$_f$:



White solid.

mp: 62°C.

IR ν_{max} (KBr): 3009, 2957, 2853, 1732, 1592, 1431, 1384, 1266, 1209, 1110, 783 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 8.14-7.36 (m, 7H), 6.42 (s, 1H), 4.56 (s, 2H), 3.83 (s, 3H), 3.68 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 160.21, 159.63, 128.69, 126.38, 126.25, 123.53, 122.72, 121.25, 120.71, 120.00, 118.58, 115.13, 115.01, 47.81, 47.49, 29.77.

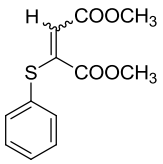
MS: *m/z* 316 (M^+).

Elemental analysis calculated for

$C_{17}H_{16}O_4S$: C, 64.54; H, 5.10; S, 10.14.

Found: C, 64.39; H, 5.04; S, 10.05.

Compound 36a:



Yellow waxy material.

IR ν_{max} (KBr): 3018, 2950, 1731, 1711, 1588, 1402, 1382, 1253, 1202, 1109 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.46-7.32 (m, 5H), 6.38 (s, 1H), 3.79 (s, 3H), 3.34 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 165.49, 164.77, 149.78, 133.36, 132.09, 129.04, 128.91, 118.87, 53.39, 52.54, 51.87.

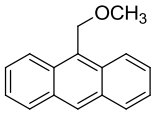
MS: *m/z* 252 (M^+).

Elemental analysis calculated for

$C_{12}H_{12}O_4S$: C, 57.13; H, 4.79; S, 12.71.

Found: C, 57.05; H, 4.70; S, 12.63.

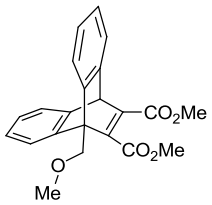
Compound 37:[51]



mp: 88-90 °C.

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

Compound 38:



White crystalline solid.

mp: 132 °C.

IR ν_{max} (KBr): 3056, 2968, 2947, 2912, 1717, 1623, 1430, 1332, 1261, 754 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.37-6.98 (m, 8H), 5.59 (s, 1H), 4.71 (s, 2H), 3.76 (s, 3H), 3.75 (s, 3H), 3.59 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 167.57, 164.07, 152.01, 145.65, 143.57, 142.79, 125.27, 125.19, 123.62, 122.16, 68.75, 59.35, 56.36, 52.33, 52.08, 50.61.

MS: *m/z* 364 (M^+).

Elemental analysis calculated for

$C_{22}H_{20}O_5$: C, 72.51; H, 5.53.

Found: C, 72.35; H, 5.44.

3.5.4.3.2. General experimental procedure for the reaction of (anthracen-9-yl)methyl sulfide (1-6) with DBA (7b).

To a 0.11 M solution of **1-6** in methanol, DBA (**7b**, 2 equivalents) was added and the mixture was refluxed. Progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was cooled and the solvent was removed under reduced pressure. The product mixture obtained was separated and purified by column chromatography on silica gel. Elution with hexane and a mixture (9:1) of hexane and dichloromethane gave **8** and **9** respectively. Elution using a mixture (4:1) of hexane and dichloromethane yielded **10**. **11** and **13** are obtained by elution with (7:3) hexane-dichloromethane mixture. Further elution with a mixture (2:3) of hexane and dichloromethane gave **(14-19)b**.

3.5.4.3.3. General experimental procedure for the reaction of (anthracen-9-yl)methyl sulfide (1 & 4) with DBE (7c).

To a solution (0.11 M) of **1/4** in methanol, DBE (**7c**, 2 equivalents) was added and the mixture was refluxed for 48h. 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 **8**, and **9** was obtained by the elution using a mixture (9:1) of hexane and dichloromethane. **10** was obtained by elution with a mixture of (4:1) hexane and dichloromethane followed by **11** and **13** were obtained by elution with (7:3) mixture of hexane and dichloromethane. Further elution with a mixture (2:3) of hexane and dichloromethane gave **14c/17c**. Here 30-37% of **1** & **4** remained unchanged in the reaction and is recovered from the reaction mixture.

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

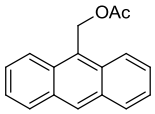
3.5.4.4.1. General experimental procedure for the reaction of (anthracen-9-yl)methyl sulfide (1-6) with DMAD (7a).

A 0.42 M solution of **1-6** in acetic acid was refluxed with DMAD (**7a**, 2 equivalents). 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 (9:1) hexane and dichloromethane gave **8** and **9** respectively. Elution with a mixture (4:1) of hexane and dichloromethane yielded **10**. **11**, **13** and **39** were obtained by the elution with a (7:3) mixture of hexane and dichloromethane. Further elution with a mixture (2:3) of hexane and dichloromethane gave **(14-19)a** and **(31-36)a**. Elution with a mixture (1:4) of hexane and dichloromethane gave **40**.

In a repeat run, a 0.042 M solution of **1-6** in acetic acid was refluxed with DMAD (2 equivalents). Most of the 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 after reaction workup was purified by column chromatography on silica gel. Products such as **8**, **9**, **10**, **11**, **13**, **(14-19)a**, **(31-36)a**, **39** and **40** were isolated.

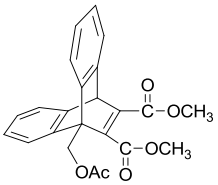
Compound 39:[61]



mp: 108-110 °C.

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

Compound 40:



White crystalline solid.

mp: 161-163 °C.

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

^{1}H NMR ($CDCl_3$): δ 7.41-7.03 (m, 8H), 5.62 (s, 1H), 5.44 (s, 2H), 3.76 (s, 3H), 3.75 (s, 3H), 2.13 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 170.62, 166.89, 163.91, 150.95, 145.42, 143.82, 142.84, 125.60, 125.30, 123.91, 121.73, 60.92, 54.84, 52.46, 52.22, 50.71, 20.62.

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

Elemental analysis calculated for

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

Found: C, 70.12; H, 4.95.

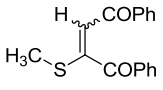
3.5.4.4.2. General experimental procedure for the reaction of (anthracen-9-yl)methyl sulfide (1-6) with DBA (7b)

To a 0.42 M solution of **1-6** in acetic acid, DBA (**7b**, 2 equivalents) was added and the mixture was refluxed. 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 and a mixture of (9:1) hexane and dichloromethane gave **8** and **9** respectively.

Elution with a mixture (4:1) of hexane and dichloromethane yielded **10**. **11**, **13** and **39** were obtained by the elution with a (7:3) mixture of hexane and dichloromethane. Further elution with a mixture (2:3) of hexane and dichloromethane gave **(14-19)b** and **(31-35)b**. In the case of (anthracen-9-yl)methyl phenyl sulfide (**6**) the product **36b** was not formed in the reaction. Elution with a mixture (1:4) of hexane and dichloromethane gave **21**. Further elution with (1:9) mixture of hexane and dichloromethane yield **20**.

In a repeat run, a 0.042 M solution of **1-6** in acetic acid with DBA (**7b**, 2 equivalents) was refluxed. The residue obtained after reaction workup was purified by column chromatography on silica gel. Similar products such as **8**, **9**, **10**, **11**, **13**, **(14-19)b**, **20**, **21**, **(31-35)b** and **39** were isolated.

Compound 31b:



Off-white crystalline solid.

mp: 60 °C.

IR ν_{max} (KBr): 3066, 2998, 2941, 2915, 1671, 1634, 1598, 1540, 1359, 1219, 1038, 783, 695 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 8.01-7.41 (m, 10H), 7.04 (s, 1H), 2.45 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 193.72, 185.14, 160.79, 137.26, 134.88, 133.60, 132.98, 128.74, 128.63, 128.47, 115.88, 14.93.

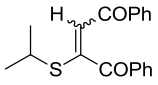
MS: *m/z* 282 (M^+).

Elemental analysis calculated for

$C_{17}H_{14}O_2S$: C, 72.31; H, 5.00; S, 11.36.

Found: C, 72.25; H, 4.91; S, 11.27.

Compound 32b:



Waxy material.

IR ν_{max} (KBr): 3066, 2967, 2926, 2869, 1671, 1629, 1590, 1531, 1380, 1245, 1110, 690 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 8.11-7.41 (m, 10H), 7.02 (s, 1H), 3.21-3.11 (m, 1H), 1.25-1.23 (d, 6H, *J*= 6.8 Hz).

^{13}C NMR ($CDCl_3$): δ 192.12, 185.27, 160.08, 130.16, 129.00, 128.83, 128.72, 128.63, 128.44, 128.13, 118.23, 37.04, 36.46, 24.13, 22.97.

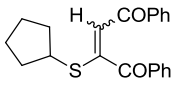
MS: *m/z* 310 (M^+).

Elemental analysis calculated for

$C_{19}H_{18}O_2S$: C, 73.52; H, 5.84; S, 10.33.

Found: C, 73.44; H, 5.73; S, 10.27.

Compound 33b:



Waxy material.

IR ν_{max} (KBr): 3066, 2966, 2930, 2867, 1670, 1625, 1592, 1535, 1360, 1247, 1116, 696 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 8.01-7.41 (m, 10H), 7.08 (s, 1H), 3.67-3.62 (m, 1H), 2.19-1.63 (m, 8H).

^{13}C NMR ($CDCl_3$): δ 193.64, 185.24, 160.91, 137.44, 135.03, 133.38, 132.86, 128.69, 128.62, 128.42, 116.59, 44.55, 33.52, 25.10.

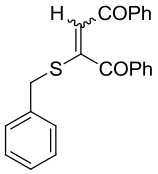
MS: *m/z* 336 (M^+).

Elemental analysis calculated for

$C_{21}H_{20}O_2S$: C, 74.97; H, 5.99; S, 9.53.

Found: C, 74.89; H, 5.91; S, 9.45.

Compound 34b:



Off-white crystalline solid.

mp: 90 °C.

IR ν_{max} (KBr): 3061, 3029, 2931, 1666, 1640, 1592, 1536, 1401, 1380, 1219, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.98-7.29 (m, 15H), 7.09 (s, 1H), 4.16 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 193.37, 185.35, 159.02, 137.18, 134.86, 134.44, 133.56, 133.01, 129.01, 128.91, 128.79, 128.77, 128.62, 128.46, 128.06, 117.06, 36.81

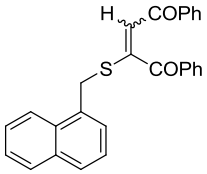
MS: *m/z* 358 (M^+).

Elemental analysis calculated for

$C_{23}H_{18}O_2S$: C, 77.07; H, 5.06; S, 8.95.

Found: C, 76.96; H, 5.00; S, 8.87.

Compound 35b:



White crystalline solid.

mp: 92°C.

IR ν_{max} (KBr): 3081, 3003, 2937, 1671, 1647, 1592, 1531, 1401, 1380, 1235, 773, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 8.09-7.25 (m, 17H), 7.09 (s, 1H), 4.32 (s, 2H).

^{13}C NMR ($CDCl_3$): δ 192.06, 188.12, 159.50, 137.81, 135.14, 134.79, 133.87, 132.74, 131.53, 131.03, 130.20, 129.11, 128.82, 128.73, 128.66, 128.40, 128.12, 126.48, 125.90, 125.18, 123.71, 116.54, 34.59.

MS: *m/z* 408 (M^+).

Elemental analysis calculated for

$C_{27}H_{20}O_2S$: C, 79.38; H, 4.93; S, 7.85.

Found: C, 79.23; H, 4.89; S, 7.79.

3.5.4.4.3. General experimental procedure for the reaction of (anthracen-9-yl)methyl sulfide (1 & 4) with DBE (7c)

To a solution (0.42 M) of **1/4** in glacial acetic acid, DBE (**7c**, 2 equivalents) was added and the mixture was refluxed for 48h. The progress of the reaction was monitored by TLC. After the reaction workup the residue obtained was purified by column chromatography on silica gel. Elution with hexane and dichloromethane mixture gave **8**, **9**, **10**, **11**, **13** and **14c/17c**. Here 40% of **1** & **4** remained unchanged in the reaction and is recovered from the reaction mixture.

3.6. References

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CHAPTER 4

PHOTOINDUCED ELECTRON TRANSFER REACTIONS OF (ANTHRACEN-9-YL)METHYL SULFIDES

4.1. Abstract

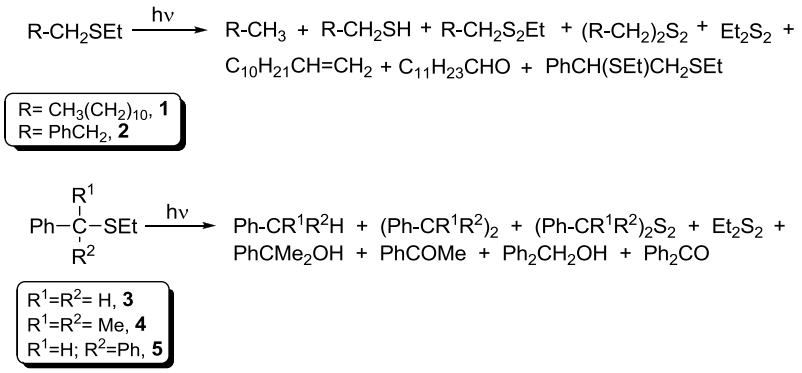
(Anthracen-9-yl)methyl sulfides undergo efficient intramolecular photoinduced electron transfer reactions to give multitude of products. Formation of different products and mechanistic details of the observed transformations are described in this chapter.

4.2. Introduction

Photooxidation of organic sulfides is of contemporary interest. Extensive studies are done on this reaction under a variety of reaction conditions, namely, (i) autooxidation,[1-3] (ii) electron transfer sensitization[4-6] and (iii) singlet oxygen oxidation.[7-10] Electron transfer reactions in solution is one of the most thoroughly investigated subjects in chemical reaction dynamics and major

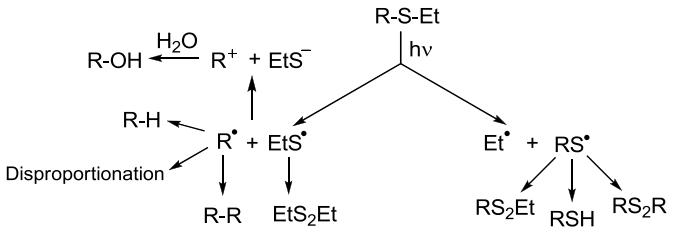
progress has been made on the field of the dependence of electron transfer rates on the free energy of reaction, on donor-acceptor distances as well as on the static properties of the solvents.[11,12] Organic sulfides undergo fast one electron oxidation reactions, owing to their relatively low ionization potentials. These sulfide radical cations decay through competitive pathways involving deprotonation at a C_α-H bond, C-S fragmentation, oxidation, aromatic substitution and dimerization by photoinduced electron transfer reaction. The relative rate constant for the reaction depend strongly on the structure of the substrate and on experimental conditions (solvent polarity, additives, etc.).[13]

For understanding the photochemistry of the C-S moiety, Bonesi *et al.* examined the irradiation of a series of ethyl sulfides RSEt, where the second *S*-bonded group is an alkyl or benzyl group.[14] With dialkyl derivative the main products were the alkane RH and the three disulfides along with some amount of alkene, aldehyde and mercaptan RSH. With benzyl derivatives such as benzyl ethyl sulfide **3** gave bibenzyl, toluene and diethyl disulphide as major products. Likewise, bicumyl, tetraphenylethane and diethyl disulfide are the important products from cumyl ethyl sulfide **4** and diphenylmethyl ethyl sulfide **5**. Furthermore, the corresponding alcohols and ketones are the minor products from **5**, but cumyl alcohol was the most abundant sulfur-free product from **4** (Scheme 4.1).[14]



Scheme 4.1

Photocleavage of the substrate and end-product formation depends upon the nature of the homolysis primary products: alkyl and alkyl sulfide radicals (Scheme 4.2). The main process from the alkyl radical $R^{\bullet}$ is hydrogen abstraction to give the alkane, or, in the case of the phenethyl radical, disproportionation to alkane and alkene takes place. Stable sulfide radicals mainly couple to form disulfides. In the case of **2** (Scheme 4.1), hydrogen abstraction from benzylic position occurs to give $PhCH^{\bullet}CH_2SEt$, which then couples with $EtS^{\bullet}$ to form $PhCH(SEt)CH_2SEt$. Formation of small amount of dodecylaldehyde is probably due to the addition of residual oxygen to the dodecyl radicals.[14]



Scheme 4.2

In the early years of 20th century, anthracene photochemistry gained much importance in the field of organic photochemistry. Mechanistic investigations on the photochemical formation of dianthracene commenced as early as 1905.[15-18] Photophysical aspects and reversibility of photodimerization reaction were studied extensively during this decade. Detailed studies on the mechanism of dimerization and on deactivation of photoexcited anthracenes by fluorescence and phosphorescence have provided fundamentally important results.[19-21] There are many reviews on the fate of electronically excited anthracenes, such as the formation of intramolecular exciplexes, twisted intramolecular charge transfer states, adiabatic cycloreversions and rotational isomerism in anthrylsubstituted ethylenes.[22-25]

In photochemical reactions, slight modifications in functional groups such as electronic and conformational configurations also have dramatic consequences. Christensen *et al.* have efficiently studied the photochemistry of sulfur-bridged anthracenes.[26] Sulfide bridged anthracene does not react in the excited state, and the sulfoxide and sulfone analogs react rapidly to form different products. Upon irradiation, sulfoxide bridged anthracene liberate SO and form bianthryl in an intramolecular fashion where as in the case of SO_2-bridged anthracene, episulfone-bridged compound is formed.

Organic thioethers and tertiary amines show efficient intramolecular and intermolecular fluorescence quenching by photoinduced electron transfer.[27] In 2002, Pedzinski *et al.* have reported the mechanism of the quenching of acridine and its

derivatives' fluorescence by sulfur-containing amino acid and carboxylic acid. The mechanism involves transfer of an electron from the sulfur atom of the quencher to acridine's lowest excited singlet state. The effect of reactant's charges on quenching rate constants was observed for the reactions of 10-methylacridinium cation with the anionic forms of the quenchers were also studied.[28]

In the present study, we have done the photochemistry of (anthracen-9-yl)methyl sulfides with inbuilt sulfide-arene unit having different electronic and steric environment around the sulfur atom. We reasoned that such substrates are potent candidates for intramolecular electron transfer reactions leading to intramolecular radical anion/radical cation pair. Further transformations of such intramolecular radical cation/radical anion pairs can lead to interesting results. In this chapter we describe the solution phase photoirradiation of different (anthracen-9-yl)methyl sulfides. Product identification and elucidation of plausible mechanism for the observed photoreactions are also reported herein.

4.3. Results and Discussion

We synthesized several (anthracen-9-yl)methyl sulfides **6-11** (Chart 4.1) having different steric and electronic environment around the sulfur atom. These compounds were synthesized for carrying out their photochemical reaction in solution phase.

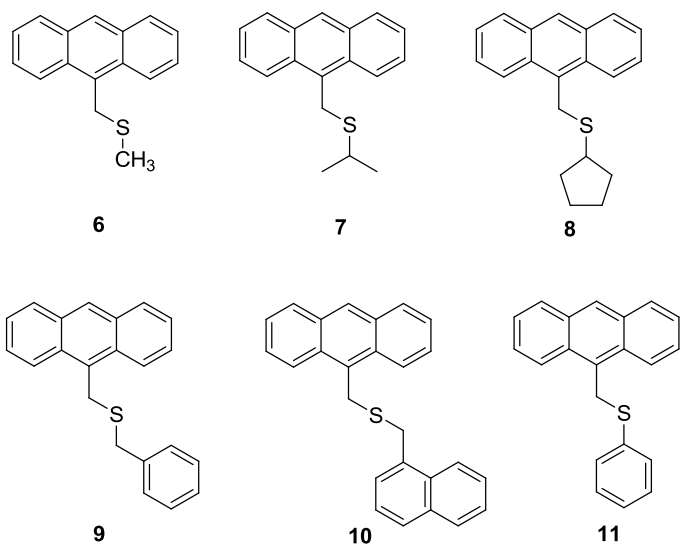


Chart 4.1. Selected (anthracen-9-yl)methyl sulfides for photochemical reaction.

We irradiated a 0.8 mmol solution of (anthracen-9-yl)methyl methyl sulfide (**6**) in dry benzene under nitrogen atmosphere using 350 nm lamps (Scheme 4.3). After completion of the reaction, solvent was removed under reduced pressure using rotary evaporator and the residue was column chromatographed. Different fractions were collected and were analyzed using spectral data. The products formed were identified as 9-methylanthracene[29] (**12**), 1,2-bis(9-anthracenyl)ethane[30-33] (**13**), lepidopterene[30,34-38] (**14**), biplanene[39-41] (**15**), 9-anthraldehyde[42] (**16**), anthrone[43] (**17**) and 9,10-anthraquinone[44] (**18**). No sulfur containing products could be isolated from the photochemical reaction of **6** since the methyl group in the sulfide part is volatile and hence could have escaped before detection. In order to analyze steric and electronic effects around the sulfur atom on the photoinduced electron

transfer reactions of (anthracen-9-yl)methyl sulfides and also to find the products corresponding to sulfide part in the photoreaction, we have carefully studied the photoreactions of **7-11** by supplying the same reaction conditions as in the reaction of **6**. All the reactions gave products identical to those obtained from **6** along with some amount of dimerization products, proton abstraction products and oxidation products of the sulfide part of different (anthracen-9-yl)methyl sulfides. The common products formed in the photoirradiation of (anthracen-9-yl)methyl sulfides (**6-11**) are shown in Chart 4.2.

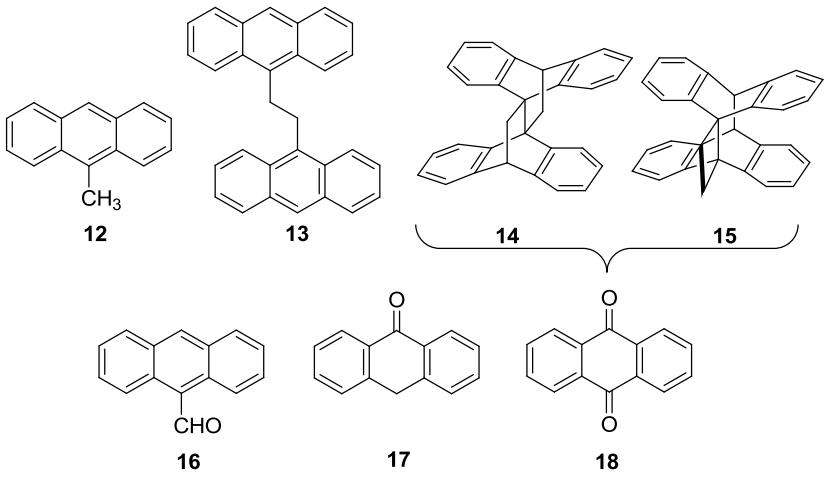
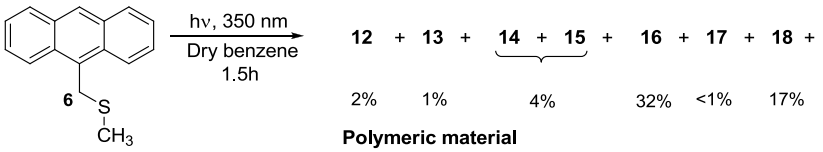
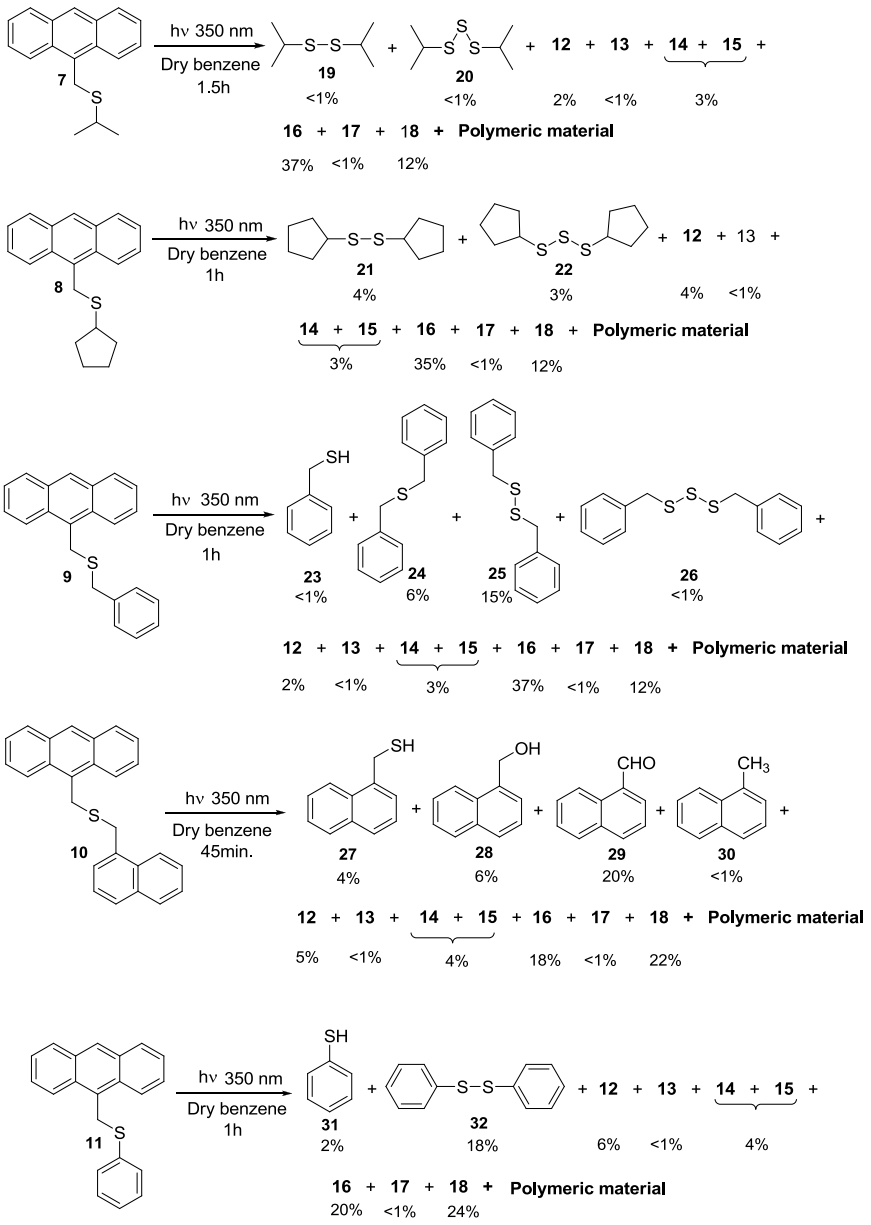


Chart 4.2. Common products formed during the photoirradiation of (anthracen-9-yl)methyl sulfides (**6-11**).



Scheme 4.3

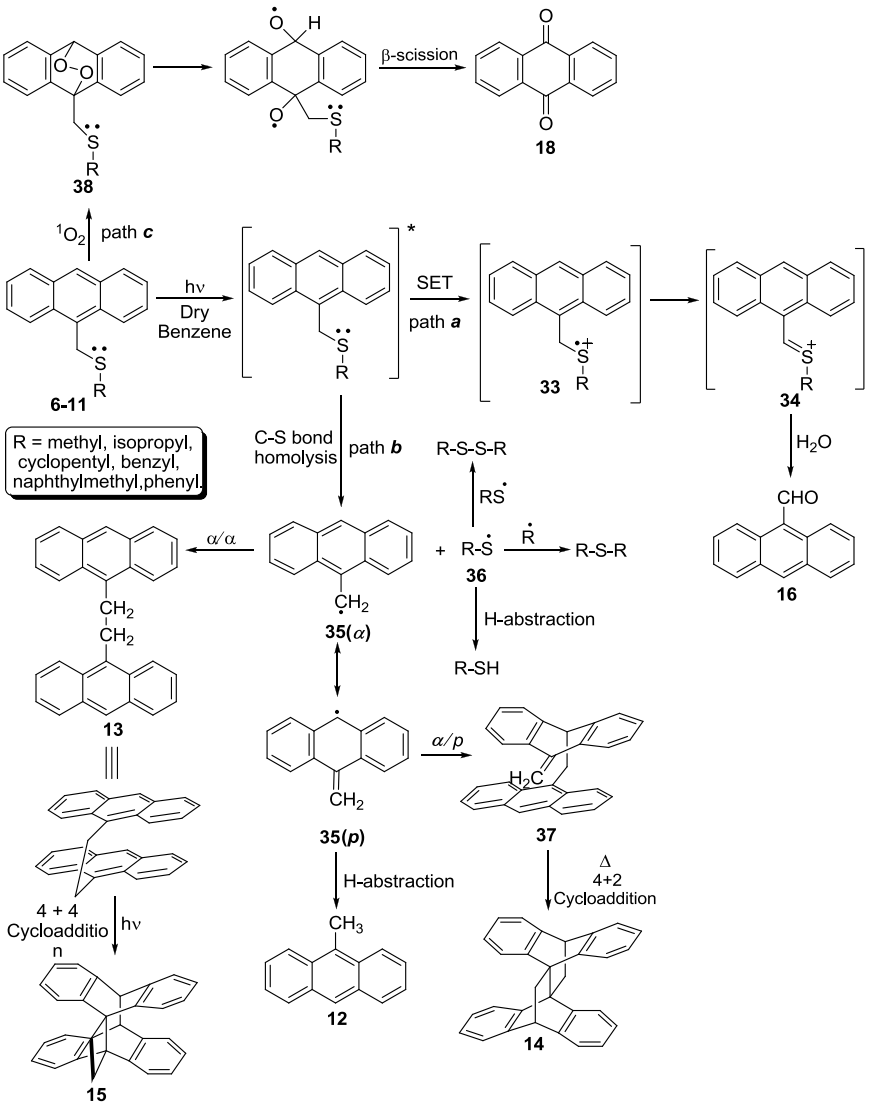
Photoirradiation of **7** gave 1,2-diisopropyl disulfide (**19**) and 1,3-diisopropyl trisulfide (**20**) as minor products along with products such as **12-18** as shown in Chart 4.2. Upon irradiation of **8** under similar photochemical conditions, products such as 1,2-dicyclopentyl disulfide (**21**) and 1,3-dicyclopentyl trisulfide (**22**) were obtained along with **12-18**. Photoproducts obtained from **9** are benzyl thiol (**23**), dibenzyl sulfide (**24**), 1,2-dibenzyl disulfide (**25**), 1,3-dibenzyl trisulfide (**26**) and **12-18**. In the case of (anthracen-9-yl)methyl naphthylmethyl sulfide (**10**) the photoproducts obtained are 1-naphthylmethylthiol (**27**), 1-naphthylmethylalcohol (**28**), 1-naphthaldehyde (**29**), 1-methylnaphthalene (**30**) and **12-18**. From the photoirradiation of (anthracen-9-yl)methyl phenyl sulfide (**11**) we got products such as thiophenol (**31**), 1,2-diphenyl disulfide (**32**) and **12-18**. Scheme 4.4 shows the complete reaction scheme for the light-induced transformations of anthracenemethyl sulfides **7-11**. Details of yield (%) of different products and time taken for the reactions are depicted in Scheme 4.4.



Scheme 4.4

Mechanism of the photochemical reaction of (anthracen-9-yl)methyl sulfides **6-11** can be explained on the basis of three

different reaction pathways depicted in Scheme 4.5. ***a***) Single electron transfer from **6**-**11** to give sulfide radical cation **33** followed by α-H atom loss and bond reorganization in **33** leading to the generation of sulfonium cation **34**. Hydrolysis of **34** gives 9-anthraldehyde (**16**). This is the major reaction pathway observed with **6**-**11**. ***b***) Homolytic photocleavage of C-S bond to give the corresponding thioalkyl (**36**) and anthracenemethyl (**35**) radicals. Further transformations of **35** leads to the formation of 9-methylanthracene (**12**) by H-abstraction, and 1,2-bis(9-anthracenyl)ethane (**13**) and lepidopterene (**14**) by dimerization. Biplanene (**15**) is formed by intramolecular photochemical (4+4) cycloaddition of (**13**). Chemistry of anthracenemethyl radical (**35**) is well documented in literature.[30,36,45] Thioalkyl radical (**36**) undergoes a series of reactions such as hydrogen atom abstraction, disproportionation reaction, dimerization reaction, oxidation reaction or alkyl radical abstraction to form a series of products such as thiols, thioethers, disulfides, aldehydes, alcohols and even trisulfides in some cases. Path ***b*** is only a minor photochemical reaction pathway exhibited by **6**-**11**. It may be mentioned here that, except in the case of **11**, loss of α' proton followed by homolytic C-S bond cleavage can also account for the generation of **35** (see Appendix 4.1).[46] Similarly, intramolecular single electron transfer (path ***a***) followed by further bond reorganization can also account for the generation of **35** and **36** (Appendix 4.2).



Scheme 4.5

We favour a mechanism involving C-S bond homolysis since this process is well documented in literature.[14] ***c***) Generation of 9,10-anthraquinone (**18**) is explained in terms of homolysis followed by β-scission of endoperoxides **38** derived from **6-11**,[47] that are formed by the reaction with *in situ* generated singlet

oxygen[48] (Scheme 4.5). Dimerization of **6-11** via a 4+4 cycloaddition pathway was not observed under the conditions employed by us.[49]

4.4. Conclusion

We have demonstrated that multiple pathways operate in the photochemical transformations of (anthracen-9-yl)methyl sulfides. These include single electron transfer mediated transformations (path ***a***), C-S bond homolysis (path ***b***) and reaction with *in situ* generated singlet oxygen (path ***c***). Based on detailed product analysis we conclude that single electron transfer and reaction with singlet oxygen are the major pathways followed by these systems.

4.5. Experimental

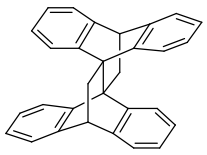
4.5.1. General Techniques

Details of general techniques are provided in the Experimental Section of Chapter 3 of this thesis. Relevent references for reported procedures and spectral data for known compounds are included in this section.

4.5.2. General Procedure for Photochemical Irradiation

A degassed solution of (anthracen-9-yl)methyl sulfides (**6-11**) (0.8 mmol) in dry benzene (200 mL) was irradiated at 350 nm lamp under argon or nitrogen atmosphere in a Rayonet photochemical reactor. Progress of the reaction was monitored by TLC. Solvent was removed under reduced pressure and the residue was column chromatographed over silica gel. Elution with hexane gave **12**. Compounds **13** and **19-32** were obtained by the elution using a mixture of (9:1) hexane and dichloromethane. Compounds **14** and **15** are obtained by the elution using (4:1) hexane-dichloromethane mixture. Elution with a mixture of (3:2) hexane and dichloromethane yielded **16**, **17** and **18**. The reaction time depends upon the nature of different (anthracen-9-yl)methyl sulfides and was indicated in Schemes 4.3 and 4.4. Presence of volatile components was examined by GC-MS analysis of the photolysate.

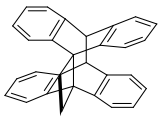
Compound 14:[35]



mp: 316-318 °C.

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

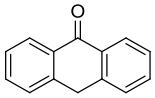
Compound 15:[32]



mp: 327-329 °C.

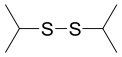
MS: *m/z* 382 (M^+).

Compound 17:[50]



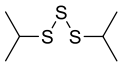
mp: 154-155 °C.
MS: 194 (M^+).

Compound 19:[51,52]



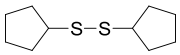
MS: *m/z* 150 (M^+).

Compound 20:[52]



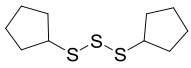
MS: *m/z* 182 (M^+).

Compound 21:[53]



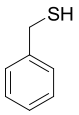
MS: *m/z* 202 (M^+).

Compound 22:[54]



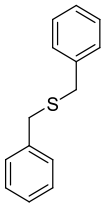
MS: *m/z* 234 (M^+).

Compound 23:[55]



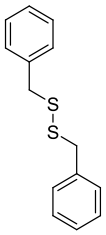
MS: *m/z* 124 (M^+).

Compound 24:[56]



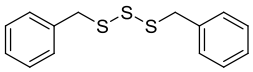
MS: *m/z* 214 (M^+).

Compound 25:[57]



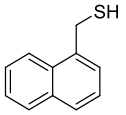
MS: *m/z* 246 (M^+).

Compound 26:[58]



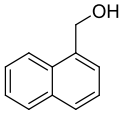
MS: *m/z* 278 (M^+).

Compound 27:[59]



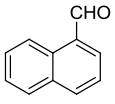
MS: *m/z* 174 (M^+).

Compound 28:[60]



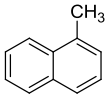
MS: *m/z* 158 (M^+).

Compound 29:[60]



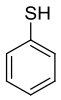
MS: *m/z* 156 (M^+).

Compound 30:[61]



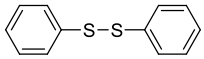
MS: *m/z* 142 (M^+).

Compound 31:[62]



MS: *m/z* 110 (M^+).

Compound 32:[62]

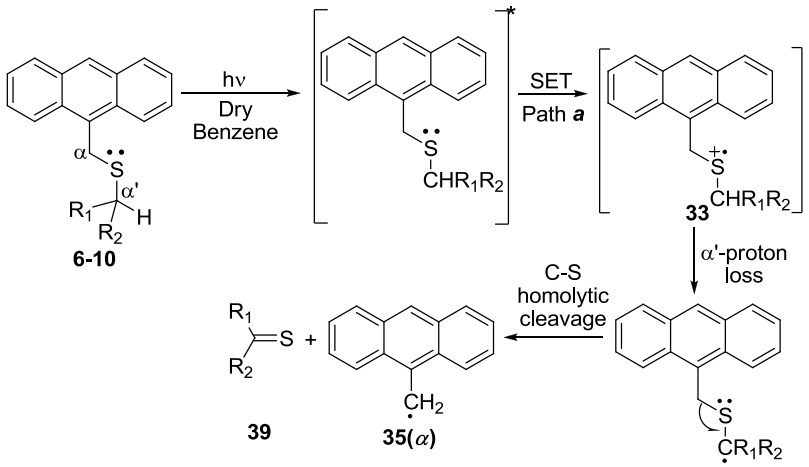


MS: *m/z* 218 (M^+).

Appendix 4.1

Alternative mechanism for the generation of (anthracen-9-yl)methyl radical (35) from (anthracen-9-yl)methyl sulfides (6-10).

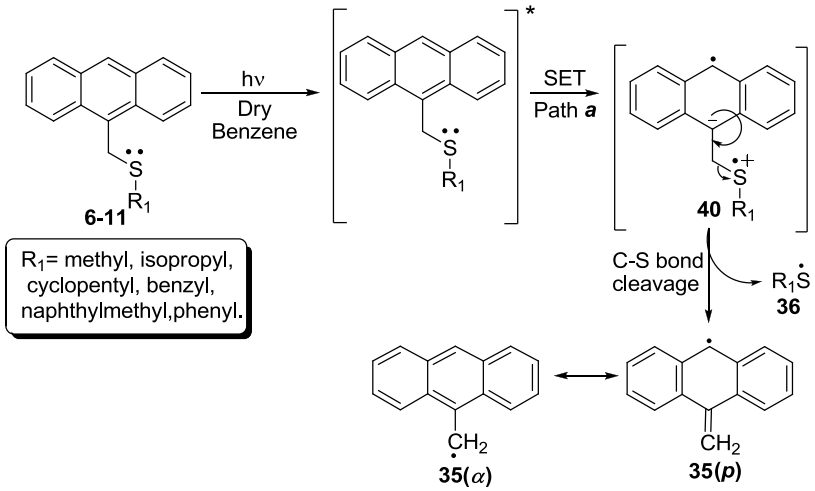
Mechanism for the photochemical generation of 9-anthracenemethyl radical (**35**) can also be explained on the basis of single electron transfer reaction (Path ***a***) of (anthracen-9-yl)methyl sulfides (**6-10**) resulting in the formation of sulfide radical cation **33** which undergo α'-proton loss from the *S*-alkyl group followed by C-S bond homolytic cleavage to form 9-anthracenemethyl radical (**35**) and thiocarbonyl compound **39**.[63] This mechanism cannot operate for **11** lacking α'-hydrogen.



Appendix 4.2

Alternative mechanism for the generation of (anthracen-9-yl)methyl radical (35) and thioalkyl radicals 36 from (anthracen-9-yl)methyl sulfides 6-11.

Mechanism of the photochemical reaction of (anthracen-9-yl)methyl sulfides **6-11** can also be explained on the basis of intramolecular one electron transfer reaction (Path ***a***) which takes place in (anthracen-9-yl)methyl sulfides to form an intramolecular sulfonium radical cation - anthracene radical anion pair **40**. This leads to the destabilization and cleavage of C-S bond to form 9-*p*-methylanthracene radical (**35*(p)***) and the corresponding sulfide radical **36**. Radical **35*(p)*** exists in equilibrium with α form of 9-methylanthracene radical **35*(α)***.



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CHAPTER 5

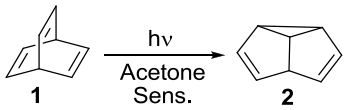
PHOTOCHEMICAL TRANSFORMATIONS OF DIBENZOBARRELENES DERIVED FROM (ANTHARCEN-9-YL)METHYL SULFIDES

5.1. Abstract

Dibenzobarrelenes or 9,10-ethenoanthracenes are known to undergo interesting photochemical transformations via singlet and triplet excited states to give dibenzocyclooctatetraene and dibenzosemibullvalenes respectively. Strong intramolecular and intermolecular fluorescence quenching was detected for organic sulfides. The present work is a systematic study of photoreactions of dibenzobarrelenes with 'inbuilt' singlet quenchers based on the assumption that organic sulfides efficiently quench singlet excited state of barrelenes by electron transfer process while leaving triplets to react freely. Upon irradiation, these sulfide appended dibenzobarrelenes gave the corresponding sulfide substituted dibenzosemibullvalenes, sulfinyl substituted dibenzosemibullvalenes and sulfonyl substituted dibenzosemibullvalenes as major products. In addition, sulfide-appended barrelenes underwent intramolecular electron transfer mediated retro Diels-Alder reaction and fragmentation reactions.

5.2. Introduction

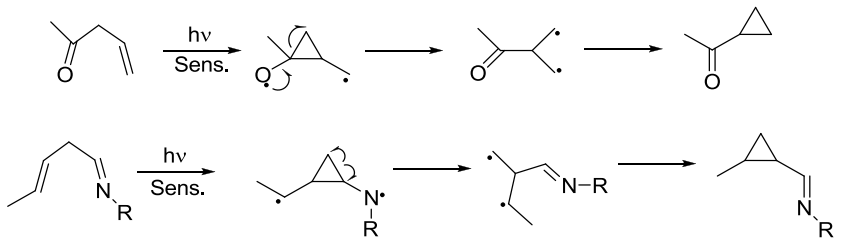
Photoisomerization of barrelene **1** to semibullvalene **2** was first reported by Zimmerman and Grunewald in 1966 (Scheme 5.1).[1] Basic structural requirement for di-π-methane rearrangement is two π systems attached to an sp^3-hybridized carbon and the reaction outcome is generation of an ene- (or aryl-) substituted cyclopropane. Zimmerman studied different aspects of di-π-methane rearrangement reaction such as the multiplicity of the excited state involved, role of the nature and stability of diradical intermediates, substituent effects, regioselectivity and stereoselectivity. He illustrated the generality of di-π-methane rearrangement (DPM) and hence this rearrangement is also referred to as the Zimmerman rearrangement.[2-5]



Scheme 5.1

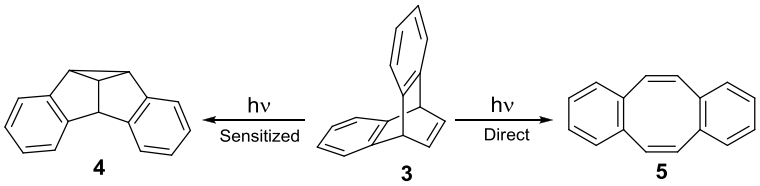
There are variations in which one of the two π-moieties is a carbonyl group that is oxa-di-π-methane rearrangement (ODPM) yielding the corresponding cyclopropyl ketone.[4-6] Similarly aza-di-π-methane rearrangement (ADPM) has a C-N double bond function

as one of the π groups, yielding exclusively the corresponding cyclopropyl imine as the product (Scheme 5.2).[4,7]



Scheme 5.2

Dibenzobarrelene **3** undergo efficient photoisomerization to give dibenzosemibullvalene **4** under sensitized irradiation and dibenzocyclooctatetraene **5** under direct irradiation (Scheme 5.3). Nature of the substituents and reaction conditions exert significant influence in controlling both product selectivity and regioselectivity of these rearrangements.[2]

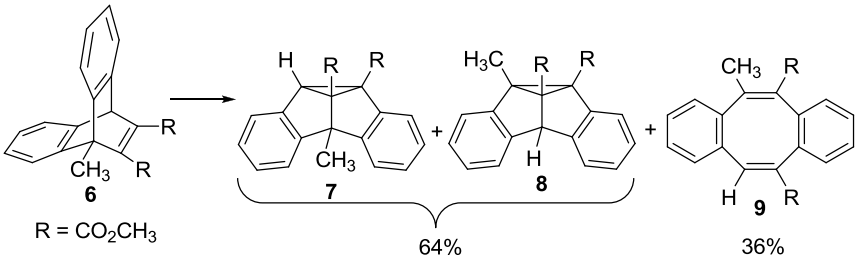


Scheme 5.3

Ciganek first studied the photochemistry of dibenzobarrelenes in solution. Photochemical studies on several dibenzobarrelenes indicated that electronic effects are important in determining the course of initial bonding in di-π-methane

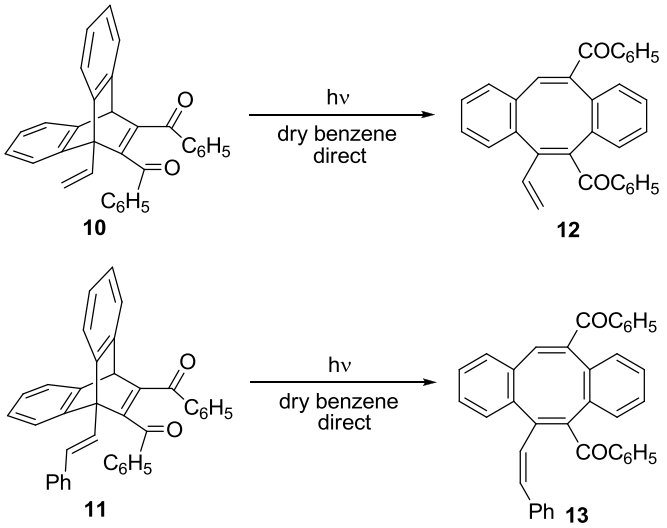
rearrangement.[8] Later, Chen reported di-π-methane rearrangement of dibenzobarrelenes in the solid state. Examination of regioselectivity of the di-π-methane photorearrangement as a function of reaction medium gives an idea about the forces that govern chemical reactivity in crystals.[9] By irradiating enantiomorphously pure crystals of a dibenzobarrelene derivative, the corresponding dibenzosemibullvalene in near quantitative enantiomeric excess was isolated.[10] Thus by measuring the absolute configurations of the reactant and its photoproduct, the absolute steric course of the rearrangement can be traced.

Triplet mediated isomerization of dibenzobarrelenes to semibullvalenes proceeds through initial "benzo-vinyl" bridging to give diradical intermediates. Direct irradiation of dibenzobarrelenes, on the other hand, leads to the formation of dibenzocyclooctatetraenes through singlet excited states which involves an intramolecular [2+2] cycloaddition reaction.[2,11] However, in reality, both singlet and triplet mediated products are formed concurrently in the direct irradiation of dibenzobarrelenes. Scheffer has reported that two isomeric semibullvalenes **7** & **8** and cycooctatetraene **9** are generated in a 64:36: ratio in the irradiation of 11,12-dicarbomethoxy substituted dibenzobarrelene **6** (Scheme 5.4).[12]



Scheme 5.4

Our group is interested in improving selectivity of barrelene photochemistry. Our major concern is: can we make barrelenes to undergo either singlet or triplet mediated transformations in a selective fashion? To this end, we examined the photochemistry of several tethered barrelenes,[13] and bridgehead olefin[14] and tertiary amine appended dibenzobarrelenes and bisdibenzobarrelenes.[15] Olefins are efficient triplet quenchers and hence efficient intramolecular triplet quenching is anticipated in the case of olefin appended dibenzobarrelenes.[16,17] Indeed, irradiation of olefin appended 11,12-dibenzoyldibenzobarrelenes **10** & **11** resulted in exclusive generation of singlet mediated dibenzocyclooctatetraene **12** & **13** owing to efficient intramolecular quenching of the triplet excited state of these dibenzobarrelenes (Scheme 5.5). Nature of both olefin appendage and substituents on barrelene chromophore plays a major role in deciding the efficiency of triplet quenching.[14]



Scheme 5.5

Since we could demonstrate intramolecular triplet quenching of dibenzobarrelenes, we explored the possibility of intramolecular quenching of singlet excited state of barrelenes. Organic thioethers and tertiary amines show efficient intramolecular and intermolecular fluorescence quenching by photoinduced electron transfer.[18] We observed efficient intramolecular electron transfer mediated singlet quenching in the case of several amine-appended dibenzobarrelenes and bisdibenzobarrelenes.[15] Neither semibullvalene nor cyclooctatetraene products were formed in the irradiation of amine appended barrelenes. However, products arising ostensibly through intramolecular electron transfer could be isolated in very low yield along with unchanged barrelenes in very high yield. This

result indicated that intramolecular electron transfer mediated quenching is more efficient than both singlet-mediated cyclooctatetraene formation and intersystem crossing to give barrelene triplets (*Note*: It is also possible that though intersystem crossing is taking place, amine component is efficiently quenching the triplet excited state as well. Transient spectroscopic studies that we have undertaken will give a definite answer for the nature of excited state quenching in the case of amine appended barrelenes). We could also demonstrate efficient photoinduced intramolecular electron transfer with anthracenemethyl sufides that is reported in Chapter 4 of this thesis. Based on these results, we reasoned that intramolecular quenching of barrelene triplet could be achieved with sulfide appended barrelenes as well. Fortunately, we had several such substrates available at hand. As an additional bonus, these barrelene substrates whose preparation is described in Chapter 3 of this thesis have strongly electron withdrawing substituents at 11,12-positions that would render them better electron acceptors.

In this chapter we describe the photochemistry of several sulfide appended dibenzobarrelenes. We have characterised the products formed in these reactions and have proposed plausible mechanisms to account for the generation of various photoproducts.

5.3. Results and Discussion

Reaction of (anthracen-9-yl)methyl sulfides with suitable electron deficient dienophiles such as DMAD and DBA in xylene, DMF or methanol yielded the corresponding 9-anthrylmethyl sulfide derived dibenzobarrelenes (Chart 5.1).[19] Since organic sulfides are efficient quenchers of singlet excited states,[18] these sulfide appended dibenzobarrelenes **14-22** are expected to undergo alternative reactions.

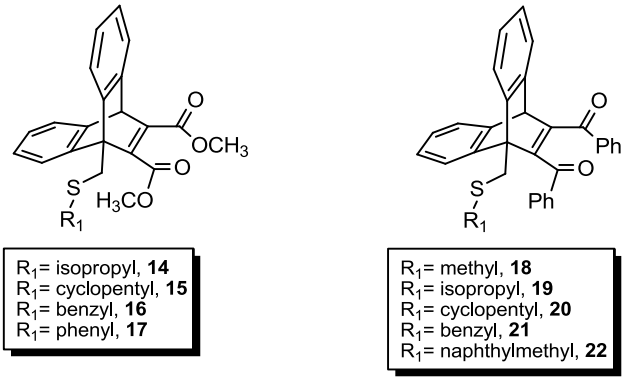
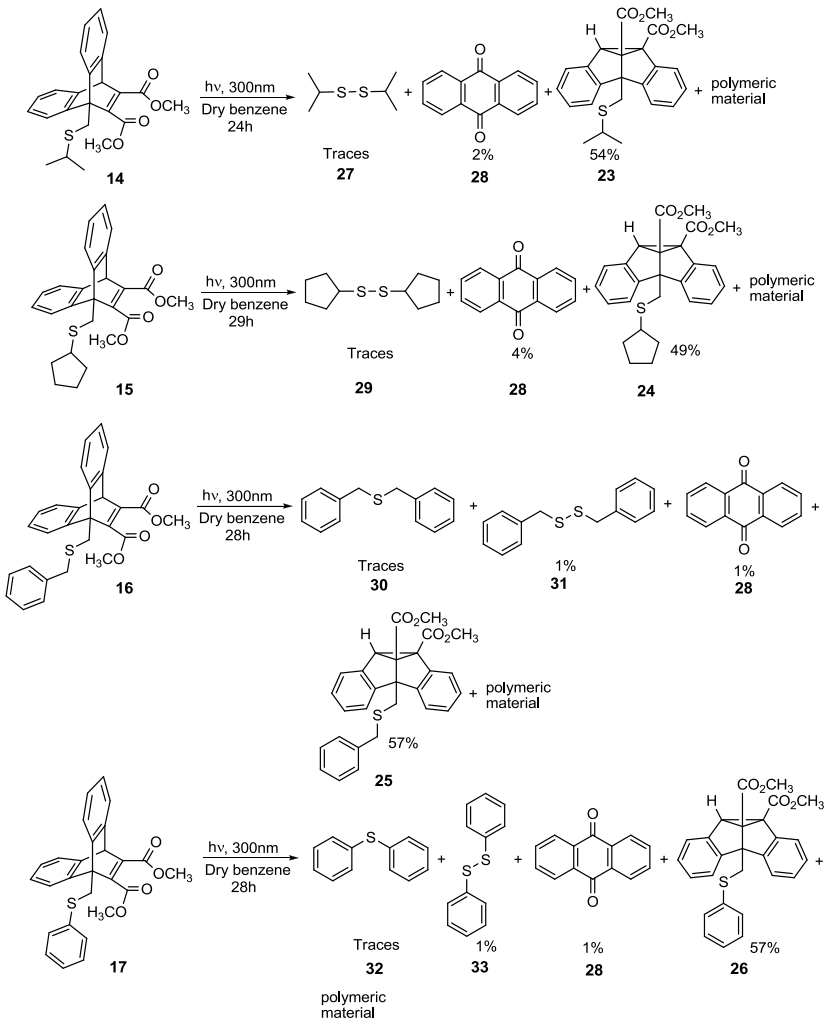


Chart 5.1. Selected 9-anthrylmethyl sulfide derived dibenzobarrelenes.

Inorder to examine quenching of singlet excited state in the photoreaction of sulfide appended dibenzobarrelenes, we irradiated 0.8 mM solution of **14-17** in dry benzene at 300 nm under nitrogen atmosphere. No cyclooctatetraene generation was observed with **14-17**. Triplet excited state mediated products such as the

corresponding sulfide appended dibenzosemibullvalenes **23-26** were obtained as the major products. Fragmentation products such as 9,10-anthraquinone (**28**)[20] and the corresponding monosulfides **30** & **32** and disulfides **27**, **29**, **31** & **33** from the sulfide part of the molecule were also formed in minor amounts. Complete reaction schemes for the photoreaction of **14-17** are shown in Scheme 5.6. Time required for the reaction and yield (%) of different products formed are depicted in Scheme 5.6. These results are in contrast with the reported generation of both cyclooctatetraene and semibullvalene products in the irradiation of barrelenes under conditions analogous to those employed by us.[12]



Scheme 5.6

Structure of dibenzosemibullvalenes **23-26** was confirmed by IR, ^{1}H NMR, ^{13}C NMR and mass spectral data. ^{1}H NMR spectrum of **23** (Figure 5.1), for example showed two doublets at δ 3.86 (1H) and δ 3.49 (1H) due to geminal protons of the methylene

group and the singlet at δ 4.30 (1H) is due to C-H proton in the cyclopropyl ring of the semibullvalene. The septet at δ 2.88 (1H) is due to the isopropyl C-H group. Two doublet at δ 1.22 (3H) and 1.19 (3H) are due to the six protons of the two diastereotopic methyl groups of isopropyl group. The singlets at δ 3.77 (3H) and δ 3.66 (3H) are due to six protons of the two carbomethoxy groups. Eight aromatic protons appeared as a multiplet in the δ 6.97-7.54 region.

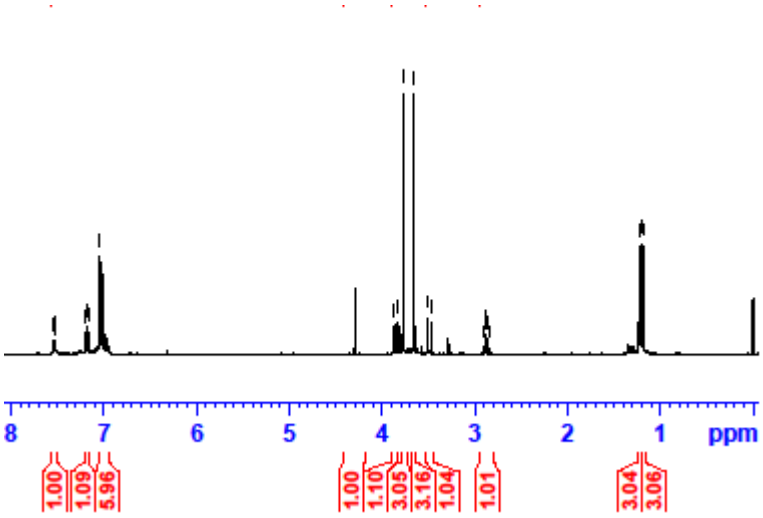
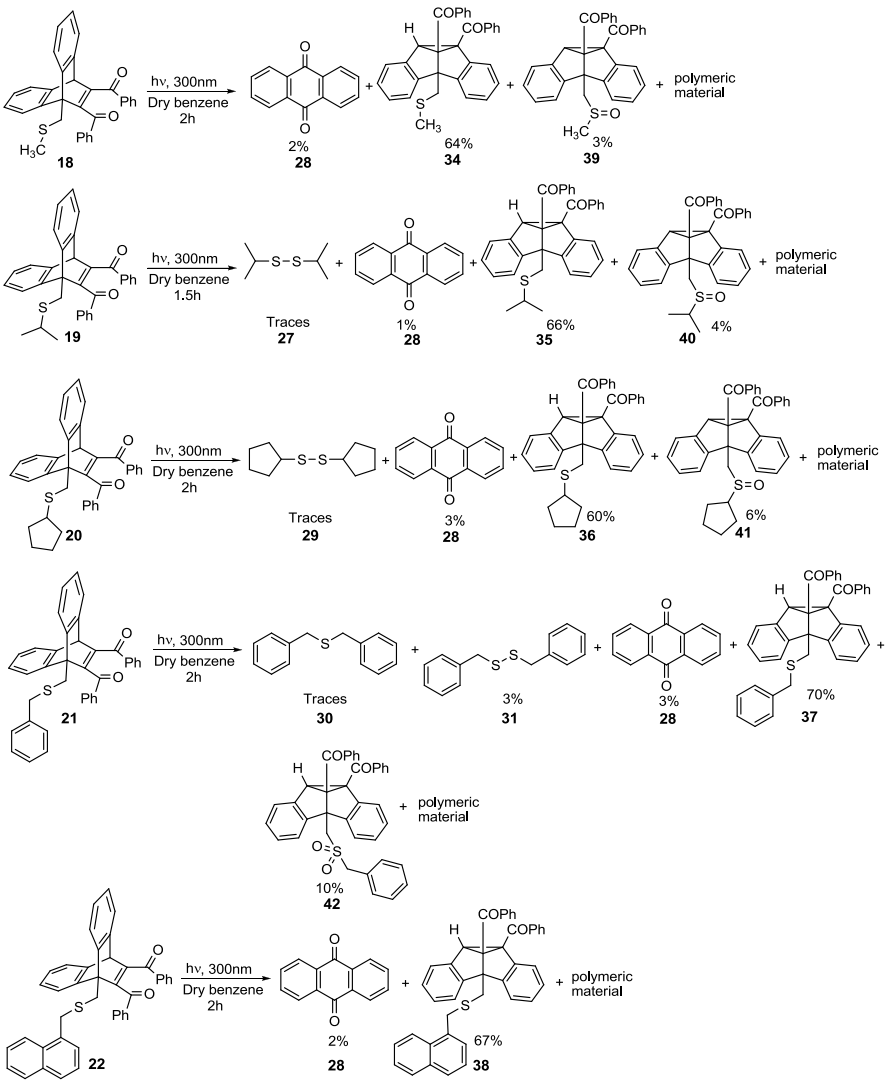


Figure 5.1. ^{1}H NMR spectrum of **23**.

In an earlier investigation, we observed that, intramolecular quenching in dibenzobarrelenes depends on the nature of substituents present in the barrelene substrate. In the photochemistry of olefin appended anthracene-DBA adducts, efficient quenching of triplet excited state was observed whereas no

quenching was found in the case of olefin appended anthracene-DMAD adducts.[14] Such diversity could be expected in the case of sulfide appended anthracene-DMAD and sulfide appended anthracene-DBA adducts as well. Based on this assumption, we examined the photoreaction of the corresponding DBA adducts **18-22** in dry benzene under identical photochemical conditions applied for **14-17**. We observed that similar products were obtained along with their oxidation products such as sulfinyl substituted dibenzosemibullvalenes **39-41** and sulfonyl substituted dibenzosemibullvalene **42** in minor amounts. The yield (%) of the major product, sulfide substituted dibenzosemibullvalenes **34-38**, is higher in comparison with that of DMAD analogue **23-26**. With sulfide appended anthracene-DBA adducts, the reactions were much faster. We conclude that sulfide apppended anthracene-DBA adducts react more efficiently than sulfide appended anthracene-DMAD adducts. More efficient intersystem crossing may be responsible for the faster reaction rates observed with these barrelenes. Complete reaction schemes for the photoreactions of **18-22** are shown in Scheme 5.7. Time required for the reactions and yields (%) of different products formed are also depicted in this scheme. In the case of methyl sulfide appended dibenzobarrelene **18**, no products corresponding to the sulfide part could be isolated.



Scheme 5.7

All products were completely characterised on the basis of spectral and analytical data. Formation of **27**, **29**, **30** and **31** are confirmed by TLC analysis and GC-MS data. Similarly,

formations of **28**, **34-42** are confirmed by IR, ^{1}H NMR, ^{13}C NMR and mass spectral data. ^{1}H NMR spectrum of **35** (Figure 5.2), for example showed two doublets at δ 3.61 (1H) and δ 3.42 (1H) due to geminal protons of the methylene group and the singlet at δ 4.65 (1H) is due to C-H proton in the cyclopropyl ring of the semibullvalene. The septet at δ 2.27 (1H) is due to the C-H proton of the isopropyl group. The two doublets at δ 1.04 (3H) and δ 0.95 (3H) are due to the six protons of the two methyl groups of isopropyl group. The eighteen aromatic protons appeared as a multiplet from δ 6.68-7.88. Structure of **35** was further confirmed by MS data which shows the molecular ion peak at *m/z* 500.

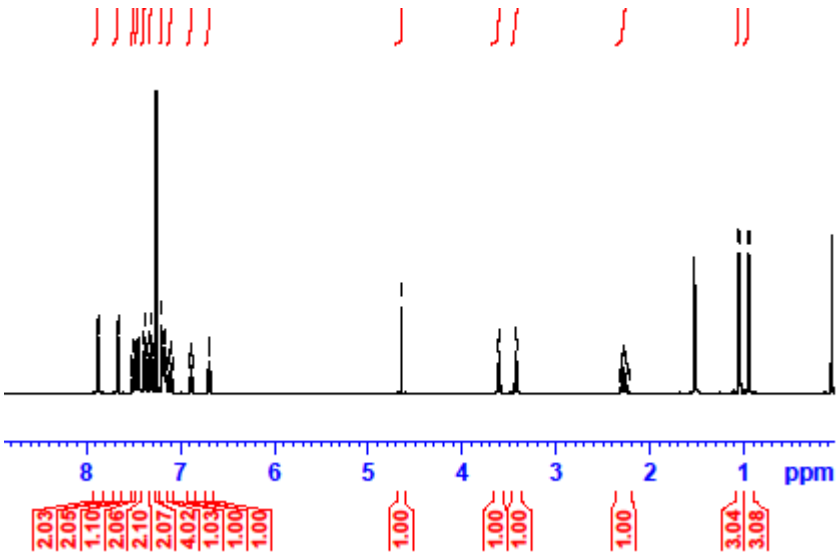


Figure 5.2. ^{1}H NMR spectrum of **35**.

^{1}H NMR spectrum of **40** (Figure 5.3) showed two doublets at δ 3.90 (1H) and δ 3.79 (1H) due to geminal protons of the methylene group and the singlet at δ 4.65 (1H) is assigned to C-H proton in the cyclopropyl ring of the semibullvalene. The septet at δ 2.46 (1H) is assigned to the C-H proton of the isopropyl group. The two doublets at δ 1.17 (3H) and δ 1.03 (3H) are due to the six protons of the two methyl groups of isopropyl group. The eighteen aromatic protons appeared as a multiplet from δ 6.71-7.88. Structure of **40** was further confirmed by MS data which shows the $(M+1)^+$ peak at *m/z* 517.

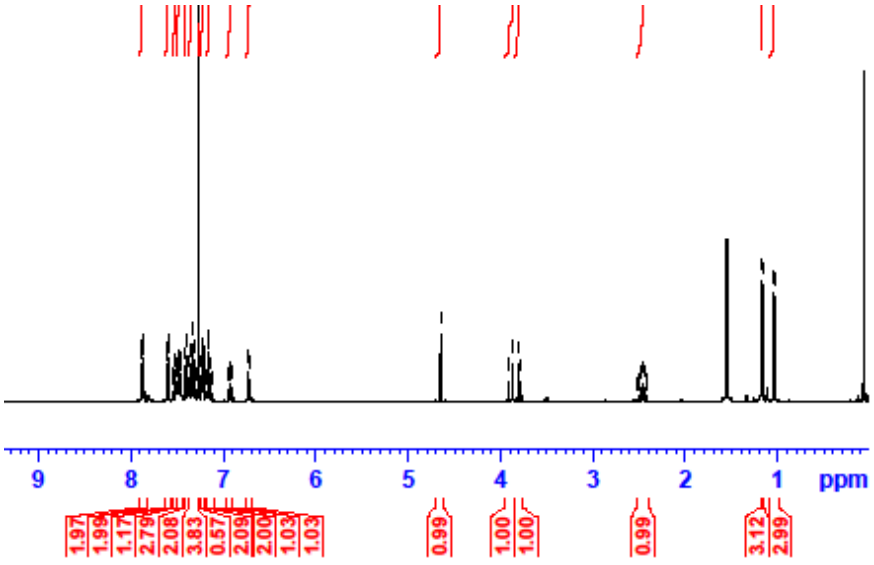


Figure 5.3. ^{1}H NMR spectrum of **40**.

In the photoirradiation of **21**, benzyl sulfonyl substituted dibenzosemibullvalene **42** was formed along with benzyl sulfide appended dibenzosemibullvalene **37** by triplet mediated pathway.

^{1}H NMR spectrum of **42** (Figure 5.4) shows two doublets at δ 4.01 (1H) and δ 3.65 (1H) due to geminal protons of the methylene group attached to the semibullvalene and the two doublets at δ 3.70 (1H) and δ 3.62 (1H) are due to methylene protons of benzyl group. The singlet at δ 4.63 (1H) is due to the C-H proton of the cyclopropyl ring in the semibullvalene structure. The twenty three aromatic protons exist as multiplet from δ 6.72- 7.89. The structure was further confirmed by MS data which shows the molecular ion peak at *m/z* 580.

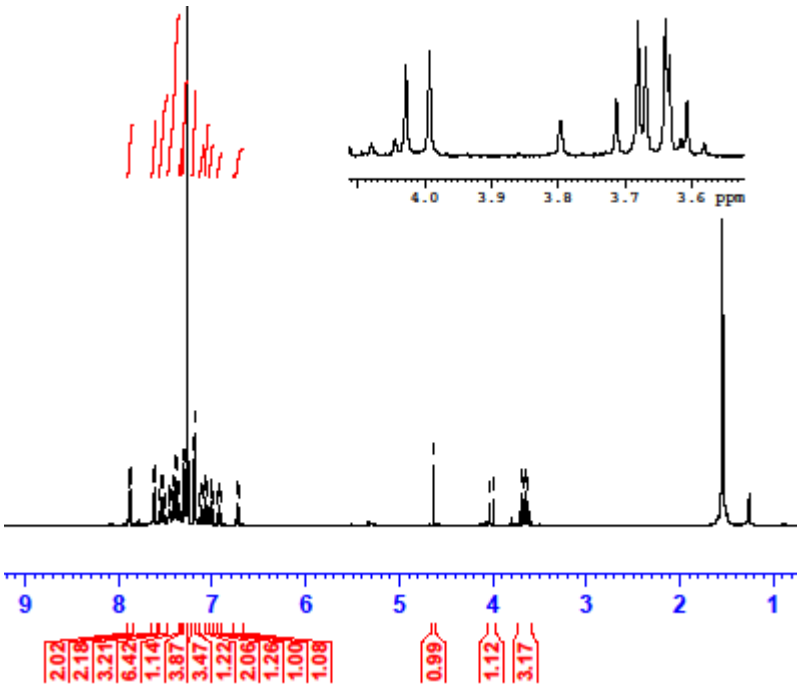


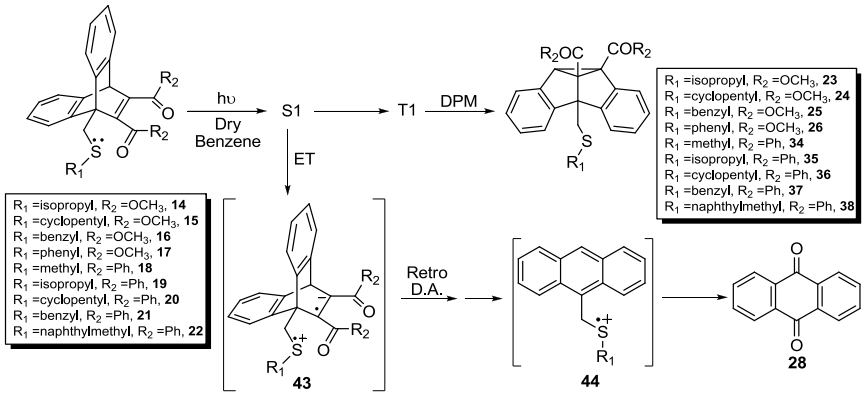
Figure 5.4. ^{1}H NMR spectrum of **42**.

Based on the results presented above, we propose the following mechanism for the photoreaction of sulfide appended dibenzobarrelenes **14-22** (Scheme 5.8). Unlike amine appended barrelenes where both singlet mediated (cyclooctatetraene) and triplet mediated (semibullvalene) reactions were completely suppressed, sulfide appended barrelenes gave triplet mediated semibullvalenes as major photoproducts. However, singlet mediated cyclooctatetraene generation is totally suppressed in this case. We reason that intersystem crossing is more efficient *vis-à-vis* intramolecular electron transfer mediated quenching in the case of sulfide appended barrelenes. Accordingly, these dibenzobarrelenes react via triplet excited state (di-π-methane rearrangement) to form sulfide appended dibenzosemibullvalenes **23-26** & **34-38**. Dibenzosemibullvalenes undergo photooxidation reaction to form sulfinyl substituted dibenzosemibullvalenes **39-41** and sulfonyl substituted dibenzosemibullvalene **42** in some cases.

Formation of 9,10-anthraquinone (**28**) albeit in negligible amounts is suggestive of intramolecular electron transfer mediated retro Diels-Alder reaction pathway reported for amine appended barrelenes.[15] It is not possible for barrelenes to give anthraquinone directly in significant quantities. Anthracenemethyl sulfides are more appropriate precursors for anthraquinone. Thus, a mechanism involving barrelene to anthracene transformation is more acceptable to account for anthraquinone generation. We propose that upon irradiation, sulfide moiety in the dibenzobarrelenes **14-22**

partially quenches the singlet excited state by photoinduced electron transfer to give intramolecular sulfide radical cation-barrelene radical anion pair **43**. Ensuing retro Diels-Alder reaction results in the formation of radical cation of anthracenemethyl sulfide[21] **44** that undergoes further dark reactions to form 9,10-anthraquinone[22] (**28**).

As in the case of anthracenemethyl sulfides reported in Chapter 4 of this thesis, products arising through C-S bond homolytic cleavage such as monosulfides (**30** & **32**) and disulfides (**27**, **29**, **31** & **33**) are also generated in very minor amounts.[21,23]



Scheme 5.8

5.4. Conclusion

We have studied efficient photochemical transformations of a few 9-anthrylmethyl sulfide derived dibenzobarrelenes. Since

organic sulfides are efficient singlet quenchers, dibenzobarrelenes with 'inbuilt' sulfide unit as singlet quencher undergo efficient triplet mediated di-π-methane rearrangement to form sulfide appended dibenzosemibullvalenes in major yields along with photooxidation products in minor yields. In some cases, sulfide appended dibenzosemibullvalenes underwent further oxidation to yield the corresponding sulfinyl and sulfonyl compounds. Efficiency of electron transfer mediated quenching appears to be influenced by other substituents present in the barrelene acceptor; in the case of 11,12-dibenzoylbarrelenes, semibullvalene formation is faster in comparison with the corresponding 11,12-dicarbomethoxy analogs. Intramolecular electron transfer followed by retro Diels-Alder reaction and C-S bond homolysis are observed as minor photoreaction pathways for sulfide appended dibenzobarrelenes.

5.5. Experimental

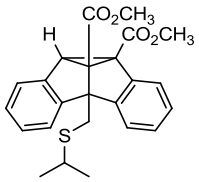
5.5.1. General Techniques

Details are provided in Chapter 3 of this thesis.

5.5.2. General Procedure for Irradiation of sulfide appended dibenzobarrelenes

A degassed solution of 9-anthrylmethyl sulfide derived dibenzobarrelenes **14-22** (0.8 mmol) in dry benzene (100 mL) was irradiated under nitrogen atmosphere using 300 nm lamps using Rayonet photochemical reactor. Progress of the reaction was monitored by TLC. Benzene was removed under reduced pressure and the residue was chromatographed over silica gel. Elution using a mixture of (9:1) of hexane and dichloromethane yielded **27**, **29**, **30**-**33**. Compound **28** was obtained by elution using (7:3) mixture of hexane and dichloromethane. Elution with a mixture (2:3) of hexane and dichloromethane yielded **23-26** & **34-38**. Also elution with a mixture (1:4) of hexane and dichloromethane yielded **39-42**. The reaction times depended on the nature of dibenzobarrelenes and are indicated in Schemes 5.6 and 5.7. Mass spectral data and the relevant references for compounds **27**, **29-33** are given in Chapter 4

Compound 23:



Waxy Material.

mp: 102 °C.

IR ν_{max} (KBr): 3061, 2978, 2947, 2859, 1718, 1593, 1437, 1386, 1312, 1261, 1214, 1064, 680 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.54-6.97 (m, 8H), 4.30 (s, 1H), 3.86 (d, 1H, *J* = 12.4 Hz), 3.77 (s, 3H), 3.66 (s, 3H), 3.49 (d, 1H, *J* = 12 Hz), 2.88 (sep, 1H, *J* = 6.4 Hz), 1.22 (d, 3H, *J* = 6.4 Hz), 1.19 (d, 3H, *J* = 6.4 Hz).

^{13}C NMR ($CDCl_3$): δ 168.04, 166.59, 149.94, 149.63, 133.54, 131.24, 126.57, 126.42, 126.39, 126.03, 124.67, 118.96, 118.40, 68.37, 65.24, 52.39, 51.55, 51.20, 48.33, 35.80, 29.22, 22.62, 22.25.

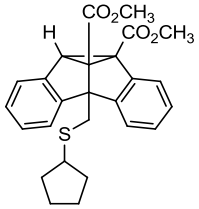
MS: *m/z* 408 (M^+).

Elemental analysis calculated for

$C_{24}H_{24}O_4S$: C, 70.56; H, 5.92; S, 7.85.

Found: C, 70.43; H, 5.88; S, 7.79.

Compound 24:



White crystalline solid.

mp: 102 °C.

IR ν_{max} (KBr): 3066, 2988, 2947, 2864, 1718, 1598, 1432, 1386, 1307, 1240, 1214, 757 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.62-7.03 (m, 8H), 4.37 (s, 1H), 3.93 (d, 1H, *J* = 12.4 Hz), 3.86 (s, 3H), 3.74 (s, 3H), 3.59 (d, 1H, *J* = 12.4 Hz), 3.14 (quin, 1H, *J* = 7.2 Hz), 2. 02-1.48 (m, 8H).

^{13}C NMR ($CDCl_3$): δ 169.10, 167.64, 151.04, 150.69, 134.61, 132.28, 127.59, 127.43, 127.41, 127.07, 125.71, 120.02, 119.44, 69.44, 66.41, 53.41, 52.58,

52.28, 49.40, 45.51, 33.99, 33.49, 31.26, 24.83, 24.81.

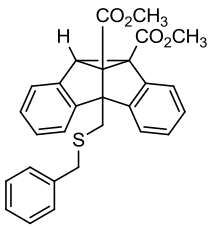
MS: *m/z* 434 (M^+).

Elemental analysis calculated for

$C_{26}H_{26}O_4S$: C, 71.86; H, 6.03; S, 7.38.

Found: C, 71.81; H, 5.94; S, 7.30.

Compound 25:



Waxy Material.

IR ν_{max} (KBr): 3030, 2972, 2952, 1727, 1593, 1401, 1380, 1302, 1261, 1214, 1069, 680 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.51-6.83 (m, 13H), 4.30 (s, 1H), 3.78 (s, 3H), 3.70 (d, 1H, *J* = 12.4 Hz), 3.67 (s, 2H), 3.63 (s, 3H), 3.47 (d, 1H, *J* = 12.4 Hz).

^{13}C NMR ($CDCl_3$): δ 167.97, 166.58, 149.84, 149.54, 137.22, 133.54, 131.25, 127.98, 127.52, 126.58, 126.52, 126.48, 126.41, 126.09, 125.94, 124.65, 118.95, 118.41, 68.29, 65.35, 52.61, 51.58, 51.29, 48.25, 36.98, 30.15.

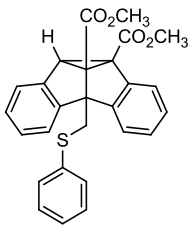
MS: *m/z* 456 (M^+).

Elemental analysis calculated for

$C_{28}H_{24}O_4S$: C, 73.66; H, 5.30; S, 7.02.

Found: C, 73.59; H, 5.23; S, 6.99.

Compound 26:



Waxy Material.

IR ν_{max} (KBr): 3038, 2965, 2940, 1729, 1588, 1428, 1382, 1315, 1266, 1212, 1069, 696 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.60-6.99 (m, 13H), 4.42 (s, 1H), 4.28 (d, 1H, *J* = 12 Hz), 4.08 (d, 1H, *J* = 12.4 Hz), 3.87 (s, 3H), 3.60 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 167.89, 166.37, 149.57, 149.26,

135.81, 133.52, 131.30, 128.88, 127.86, 126.64, 126.56, 126.53, 126.47, 125.99, 125.31, 124.68, 119.05, 118.47, 68.37, 65.06, 52.78, 51.61, 51.31, 48.21, 33.19.

MS: *m/z* 442 (M^+).

Elemental analysis calculated for

$C_{27}H_{22}O_4S$: C, 73.28; H, 5.01; S, 7.25.

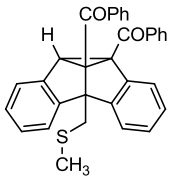
Found: C, 73.21; H, 4.93; S, 7.17.

Compound 34:

White crystalline solid.

mp: 176 °C.

IR ν_{max} (KBr): 3060, 2978, 2910, 2859, 1681, 1660, 1598, 1401, 1380, 1266, 1245, 1069, 1012, 696 cm^{-1}.



^{1}H NMR ($CDCl_3$): δ 7.89-6.70 (m, 18H), 4.65 (s, 1H), 3.60 (d, 1H, *J* = 12.4 Hz), 3.33 (d, 1H, *J* = 12.4 Hz), 1.72 (s, 3H).

^{13}C NMR ($CDCl_3$): δ 195.81, 195.32, 150.28, 148.37, 138.01, 137.11, 135.46, 135.10, 132.65, 132.55, 130.18, 128.88, 128.14, 127.75, 127.69, 127.45, 127.32, 126.59, 125.99, 119.96, 119.86, 67.67, 60.71, 47.87, 34.65, 17.00.

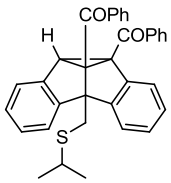
MS: *m/z* 472 (M^+).

Elemental analysis calculated for

$C_{32}H_{24}O_2S$: C, 81.33; H, 5.12; S, 6.78.

Found: C, 81.21; H, 5.04; S, 6.69.

Compound 35:



White crystalline solid.

mp: 178 °C.

IR ν_{max} (KBr): 3066, 2972, 2952, 2858, 1681, 1655, 1593, 1396, 1307, 1251, 1074, 695 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.89-6.68 (m, 18H), 4.65 (s, 1H), 3.61 (d, 1H, *J* = 12 Hz), 3.42 (d, 1H, *J* = 12.4 Hz), 2.28 (sep, 1H, *J* = 6.8 Hz), 1.05 (d, 3H, *J* = 6.8 Hz), 0.95 (d, 3H, *J* = 6.8 Hz).

^{13}C NMR ($CDCl_3$): δ 195.90, 195.01, 151.52, 150.46, 137.97, 137.15, 135.47, 135.11, 132.60, 132.56, 130.19, 129.04, 128.11, 128.06, 127.71, 127.43, 127.26, 126.59, 125.96, 119.96, 119.85, 67.39, 60.66, 47.96, 36.98, 30.95, 23.14, 22.83.

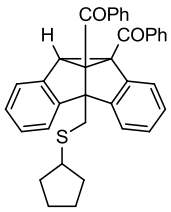
MS: *m/z* 500 (M^+).

Elemental analysis calculated for

$C_{34}H_{28}O_2S$: C, 81.57; H, 5.64; S, 6.40.

Found: C, 81.52; H, 5.58; S, 6.33.

Compound 36:



White crystalline solid.

mp: 154 °C.

IR ν_{max} (KBr): 3061, 2962, 2928, 2858, 1676, 1660, 1592, 1401, 1390, 1261, 1110, 1074 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.89-6.68 (m, 18H), 4.65 (s, 1H), 3.63 (d, 1H, *J* = 12.4 Hz), 3.41 (d, 1H, *J* = 12.4 Hz), 2.50 (quin, 1H, *J* = 6.8 Hz), 1.74-1.22 (m, 8H).

^{13}C NMR ($CDCl_3$): δ 196.55, 194.84, 154.16, 151.89, 137.94, 137.13, 135.44, 135.08, 132.57, 130.18, 129.03, 128.09, 128.02, 127.67, 127.41, 127.23, 126.58, 125.94, 119.96, 119.85, 67.40, 60.64, 47.92, 45.47, 33.37, 33.08, 31.99, 24.66.

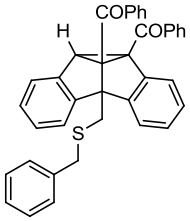
MS: *m/z* 526 (M^+).

Elemental analysis calculated for

$C_{36}H_{30}O_2S$: C, 82.10; H, 5.74; S, 6.09.

Found: C, 82.03; H, 5.67; S, 6.03.

Compound 37:



White crystalline solid.

mp: 148 °C.

IR ν_{max} (KBr): 2973, 2956, 2861, 1676, 1655, 1598, 1406, 1385, 1307, 1266, 1131, 1069, 696 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.89-6.70 (m, 23H), 4.65 (s, 1H), 3.50 (d, 1H, *J* = 12.8 Hz), 3.33 (d, 1H, *J* = 12.8 Hz), 3.31 (d, 1H, *J* = 12.8 Hz), 3.22 (d, 1H, *J* = 12.8 Hz).

^{13}C NMR ($CDCl_3$): δ 195.84, 195.12, 151.25, 150.28, 137.91, 137.64, 137.09, 135.37, 135. 01, 132.69, 132.66, 130.17, 129.07, 128.43, 128.27, 128.14, 127.74, 127.67, 127.42, 127.29, 127.00, 126.56, 125.93, 119.98, 119.88, 67.53, 60.68, 47.95, 37.99, 31.95.

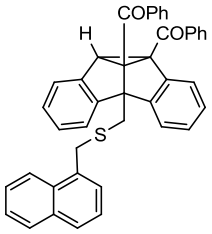
MS: *m/z* 548 (M^+).

Elemental analysis calculated for

$C_{38}H_{28}O_2S$: C, 83.18; H, 5.14; S, 5.84.

Found: C, 83.09; H, 5.08; S, 5.78.

Compound 38:



White crystalline solid.

mp: 126 °C.

IR ν_{max} (KBr): 3058, 2973, 2926, 2848, 1676, 1660, 1593, 1401, 1385, 1302, 1266, 1136, 1064, 696 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.88-6.67 (m, 25H), 4.65 (s, 1H),

3.82 (d, 1H, *J* = 13.2 Hz), 3.72 (d, 1H, *J* = 13.2 Hz), 3.59 (d, 1H, *J* = 12.8 Hz), 3.42 (d, 1H, *J*= 12.4 Hz).

^{13}C NMR ($CDCl_3$): δ 195.01, 194.89, 151.34, 150.29, 137.82, 137.05, 135.35, 134.97, 133.92, 133.14, 132.65, 130.17, 129.06, 128.60, 128.26, 128.15, 128.09, 127.70, 127.66, 127.40, 127.26, 126.96, 126.55, 126.05, 125.89, 125.77, 125.07, 123.95, 120.01, 119.87, 67.64, 60.68, 47.97, 35.75, 32.28.

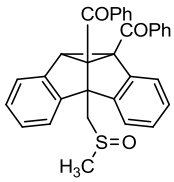
MS: *m/z* 598 (M^+).

Elemental analysis calculated for

$C_{42}H_{30}O_2S$: C, 84.25; H, 5.05; S, 5.36.

Found: C, 84.19; H, 5.01; S, 5.28.

Compound 39:

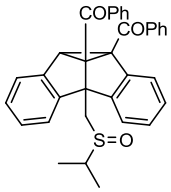


White crystalline solid.

IR ν_{max} (KBr): 3041, 2978, 2848, 1681, 1598, 1401, 1380, 1307, 1261, 1136, 1064, 680 cm^{-1}.

MS: *m/z* 488 (M^+).

Compound 40:



White crystalline solid.

mp: 198 °C.

IR ν_{max} (KBr): 3061, 2973, 2916, 2858, 1676, 1652, 1598, 1401, 1380, 1308, 1266, 1069, 696 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.88-6.71 (m, 18H), 4.65 (s, 1H), 3.89 (d, 1H, *J* = 13.6 Hz), 3.79 (d, 1H, *J* = 14 Hz), 2.46 (sep, 1H, *J* = 6.8 Hz), 1.17 (d, 3H, *J* = 6.8 Hz), 1.03 (d, 3H, *J* = 6.8 Hz).

^{13}C NMR ($CDCl_3$): δ 195.49, 194.01, 149.18, 148.70,

137.14, 135.71, 133.63, 131.98, 131.73, 129.04, 128.00, 127.38, 127.31, 126.97, 126.78, 126.69, 126.54, 125.50, 124.56, 120.94, 119.21, 63.32, 60.94, 50.00, 48.98, 47.79, 15.59, 12.02.

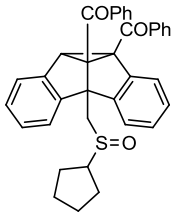
MS: *m/z* 517 $(M+1)^+$.

Elemental analysis calculated for

$C_{34}H_{28}O_3S$: C, 79.04; H, 5.46; S, 6.21.

Found: C, 78.94; H, 5.33; S, 6.15.

Compound 41:



White crystalline solid.

mp: 188 °C.

IR ν_{max} (KBr): 2962, 2926, 2858, 1666, 1593, 1401, 1381, 1322, 1111, 1074 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.88-6.72 (m, 18H), 4.65 (s, 1H), 3.91 (d, 1H, *J* = 14 Hz), 3.80 (d, 1H, *J* = 14 Hz), 2.74 (quin, 1H, *J* = 6.8 Hz), 1.74-1.22 (m, 8H).

^{13}C NMR ($CDCl_3$): δ 196.49, 195.04, 150.31, 149.73, 138.24, 134.63, 133.99, 133.01, 132.75, 130.06, 129.03, 128.39, 128.35, 127.94, 127.74, 127.55, 126.53, 125.54, 122.00, 64.44, 61.96, 60.55, 51.69, 48.79, 27.77, 26.01, 25.65, 23.88.

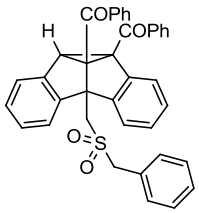
MS: *m/z* 543 $(M+1)^+$.

Elemental analysis calculated for

$C_{36}H_{30}O_3S$: C, 79.67; H, 5.57; S, 5.91.

Found: C, 79.58; H, 5.53; S, 5.83.

Compound 42:



White crystalline solid.

mp: 196 °C.

IR ν_{max} (KBr): 3061, 2973, 2916, 2858, 1676, 1652, 1598, 1401, 1380, 1266, 1069, 696 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ 7.89-6.72 (m, 23H), 4.63 (s, 1H), 4.01 (d, 1H, *J* = 14 Hz), 3.70 (d, 1H, *J* = 14 Hz), 3.65 (d, 1H, *J* = 14 Hz), 3.62 (d, 1H, *J* = 14 Hz).

^{13}C NMR ($CDCl_3$): δ 197.21, 196.19, 175.87, 174.47, 167.69, 167.19, 156.72, 134.39, 132.19, 129.11, 128.03, 127.71, 122.62, 113.04, 101.60, 57.45, 42.04, 39.94, 32.70, 18.92.

MS: *m/z* 580 (M^+).

Elemental analysis calculated for

$C_{38}H_{28}O_4S$: C, 78.60; H, 4.86; S, 5.52.

Found: C, 78.51; H, 4.79; S, 5.48.

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List of Publications

Journal Publications

- Dramatic solvent and concentration dependence in the reaction of (anthracen-9-yl)methanamines with suitable electron-deficient acetylenes, Jomon P. Jacob, **Reshma Gopalakrishnan**, Rekha R. Mallia, Jean John Vadakkan, Perupparampil A. Unnikrishnan and Sreedharan Prathapan, *J. Phys. Org. Chem.* **2014**, *27*, 884–891.

- Facile one–pot method for the synthesis of arylmethanamines, Jomon P. Jacob, Ligi M. Lalu, **Reshma Gopalakrishnan**, Rekha R. Mallia, Sreedharan Prathapan and Perupparampil A. Unnikrishnan, *Journal of Advanced Research in Applied Chemistry & Chemical Engineering* (Accepted).

- Solvent effects in the reaction between (anthracen-9-yl)methyl sulfides and electron deficient acetylenes, **Reshma Gopalakrishnan**, Jomon P. Jacob, Rekha R. Mallia, Perupparampil A. Unnikrishnan and Sreedharan Prathapan, *J. Phys. Org. Chem.* (Communicated)

- Efficient one-pot synthesis of (anthracen-9-yl)methyl sulfane derivatives, **Reshma Gopalakrishnan**, Jomon P. Jacob, Perupparampil A. Unnikrishnan and Sreedharan Prathapan, *Cogent Chemistry* (Communicated).

- Photoinduced electron transfer reactions of a few (anthracen-9-yl)methanamines, Jomon P. Jacob, **Reshma Gopalakrishnan**, Rekha R. Mallia, Perupparampil A. Unnikrishnan and Sreedharan Prathapan, *J. Photochem. Photobiol., A* (Communicated)

Conference Presentations

- Photoinduced electron transfer reaction of (anthracen-9-yl)methyl methyl thioether, **G. Reshma**, J. P. Jacob, P. A. Unnikrishnan, N. Manoj and S. Prathapan *Current Trends in Chemistry (Ctric 2013)*, Department of Applied Chemistry, Cochin University of Science and Technology, Cochin, March **2013**.

- Studies on the Solvent Dependence in the Reaction of (Anthracen-9-yl)methyl benzyl thioether with DMAD, **G. Reshma**, J. P. Jacob, P. A. Unnikrishnan, N. Manoj and S. Prathapan *Current Trends in Chemistry (Ctric2014)*, Department of Applied Chemistry, Cochin University of Science and Technology, Cochin, January **2014**.

- Studies on the Solvent Dependence in the Reaction of (Anthracen-9-yl)methyl methyl thioether with DBA, **G. Reshma**, J. P. Jacob, P. A. Unnikrishnan, N. Manoj and S. Prathapan *National Seminar on 'Frontiers in Chemistry-2014',* Al-Ameen College, Edathala.