SOME ASPECTS OF CHEMISTRY OF THIOAMIDE VINYLOGS, N,N-DIMETHYL-N'-THIOBENZOYLFORMAMIDINES AND RELATED SYSTEMS

By

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A THESIS

SUBMITTED

IN

FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

To

THE NORTH-EASTERN HILL UNIVERSITY

SHILLONG-793 001

MEGHALAYA (INDIA)

JANUARY, 1989

Dedicated

to

my beloved

Parent

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Grams : NEHU

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Dr. M.P. Mahajan
Reader
Department of Chemistry

CERTIFICATE

This is to certify that the work desceribed in this thesis has been carried out by Mr. Parag Dhar Baruah under my supervision. He has satisfactorily completed the Pre-Ph.D. courses prescribed and the period of two years of investigational work for the award of Ph.D. degree in Chemistry.

The work described in this thesis is original and has not been submitted for any other degree or diploma in this or any other University.

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This is to certify that Mr. Parag Dhar Baruah, a Ph.D. student of the Department of Chemistry has satisfactorily completed the following courses as a part of his Ph.D. course programme.

Course No.	Title
1. Chem - 624	Pericyclic Reactions
2. Chem - 668	Electrochemistry
3. SPS - 601	French Language
4. SPS - 630	Experimental Techniques

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A C K N O W L E D G E M E N T

The research work described in this thesis was carried out in the Department of Chemistry, North-Eastern Hill University, Shillong under the supervision of Dr. M.P. Mahajan and I take this opportunity to thank him for suggesting the problem and for his able guidance throughout the entire course of this investigation.

I am very much thankful to the Head of the Department, Chemistry, NEHU and all the faculty members of the Department who have been extremely helpful during my stay. I wish to thank in particular Dr. R.K. Poddar and Prof. M.K. Choudhury who took care of day-to-day problems concerning my work during the absence of Dr. M.P. Mahajan.

I am very much grateful to Dr. J.P. Pradère, Nantes,CEDEX, France and Prof. G. Singh, Chemistry Department, NEHU for helping me to obtain PMR and ^{13}C NMR spectra of various compounds. My thanks are due also to the Directors and Technicians of the Regional Sophisticated Instrumentation Centre and Central Drug Research Institute, Lucknow and North-Eastern Hill University, Shillong for providing the spectral and analytical data of compounds described in this thesis. The financial assistance from the Council of Scientific and Industrial Research, New Delhi is gratefully acknowledged.

I am extremely grateful to Mr. S.N. Mazumder, Lecturer, St. Edmund's College and Miss S. Mukherjee, Lecturer, Lady Keane's College for their constant co-operation and help throughout the course of my research work.

It is a great pleasure for me to thank all the research scholars and friends in the Department who have been of invaluable help to me. I wish to mention in particular Mr. M. Bhattacharjee, Mr. P. Paul, Mr. C.R. Bhattacharjee, Mr. R. Gupta, Mr. B. Paul, Mr. R. Chakravorty, Mr. S. Sarkar, Mr. A. Dey, Mr. D. Dey, Mr. J.P. Baruah and Mr. P.C. Sarma who made my stay extremely pleasant.

I express my sincere gratitude to Mr. Biplab Nag, JRF who took the pain of drawing the various schemes mentioned in the thesis.

I am grateful to Mrs. Rajamma K. for meticulous typing of the manuscript and to Mrs. Florency Joseph for efficient photocopying of the same.

Finally I acknowledge the debt I owe to my parents and family members for their support, patience and encouragement throughout this investigation.

Parag Dhar Baruah

PARAG DHAR BARUAH

C O N T E N T S

P R E F A C E

The heterodienes are of great interest to organic chemists because of the important role they play in synthetic organic chemistry. Their study has illuminated many aspects of synthetic and mechanistic chemistry. The chemistry of thioamide vinylogs and related compounds has developed enormously over the last ten to fifteen years. The synthetic scope of these versatile synthons still remains unexploited to a considerable extent. This dissertation reports the reactions of thioamide vinylogs and related compounds with dienophiles, heterodienophiles and other potential heterodienes.

A brief survey of reports concerning the chemistry and synthetic versatility of thioamide vinylogs and related compounds is presented in chapter I.

Chapter II concerns the reactions of thioamide vinylogs with ethyl azodicarboxylate. The formation of various substituted thiadiazines in these reactions has been substantiated with the help of ^{13}C NMR, PMR and analytical data.

Chapter III describes the reactions of thioamide vinylogs with nitroalkenes, nitrosoalkenes, dicyclopentadiene and norbornylene. The structures assigned to products have been supported by spectral and analytical evidences.

Chapter IV deals with the reactions of thioamide vinylogs with isonitriles and isothiocyanates and the reactions of N,N-dimethyl-

N'-thiobenzoylformamidines and N,N-dimethyl-N'-phenylthiocarbamoylformamidines with N-arylbenzimidoyl chlorides. Mechanistic pathways leading to the formation of various products have also been discussed.

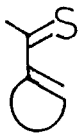
The entire documentation in this thesis is supported by appropriate references.

CHAPTER I

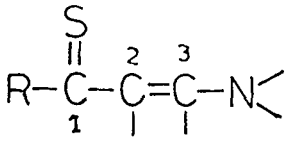
INTRODUCTION

The cyclenic α,β-ethylenic thioketones (1) are known to be relatively stable. However the acyclic α,β-ethylenic thioketones are unstable and are known to polymerise rapidly[1]. The conjugation of the two π bonds with the lone pair of a hetero atom (S,N.....) stabilises the corresponding ethylenic thioketones[2] by a push pull effect between the electron donor nitrogen and electron acceptor the thiocarbonyl.

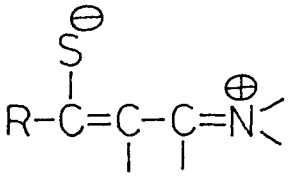
The ß-aminovinylthioketones 2 are examples of this and are



1



2a



2b

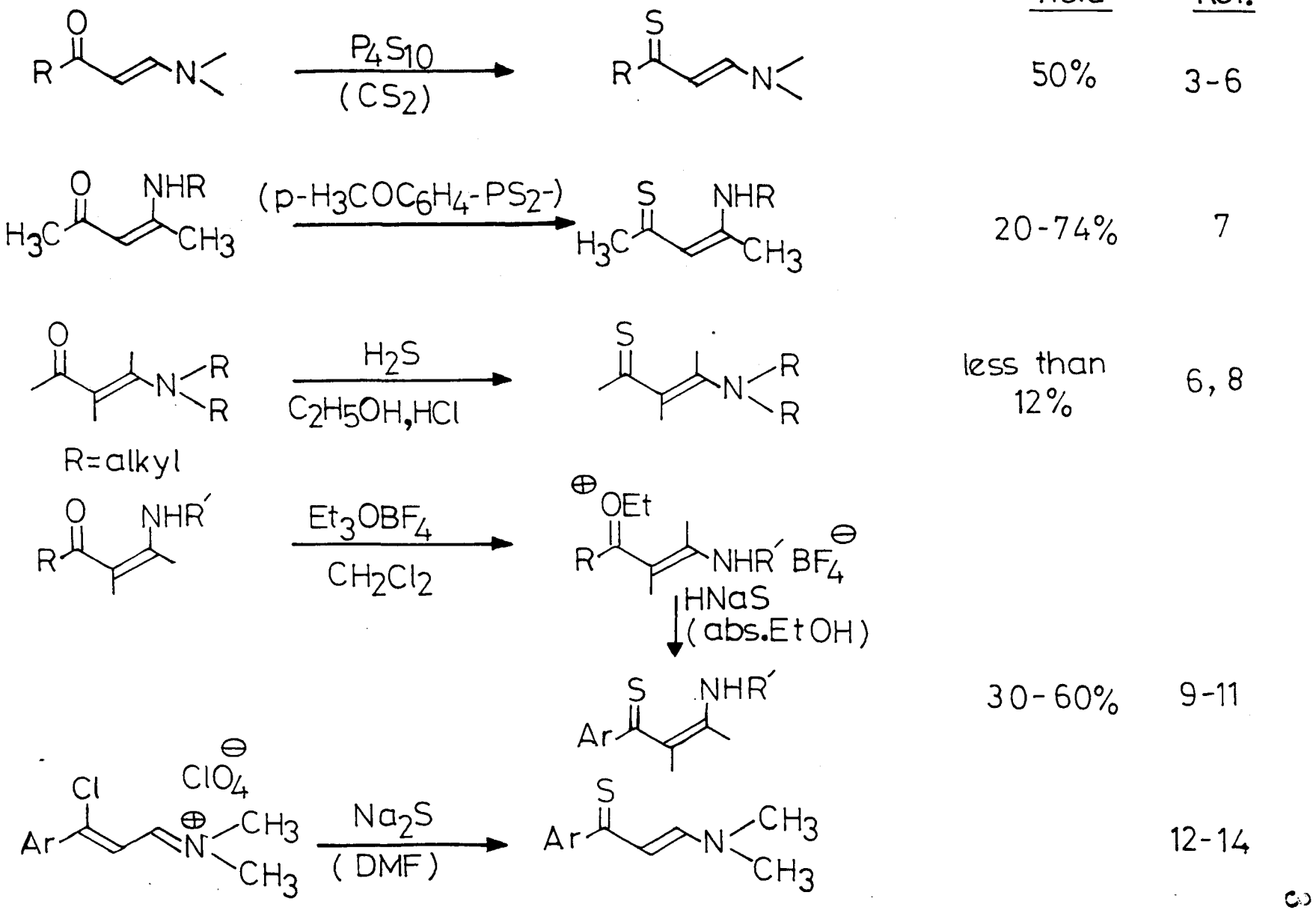
referred to as "thioamide vinylogs" or "enamino-thiones" in this thesis.

Synthesis of the thioamide vinylogs/enamino-thiones:

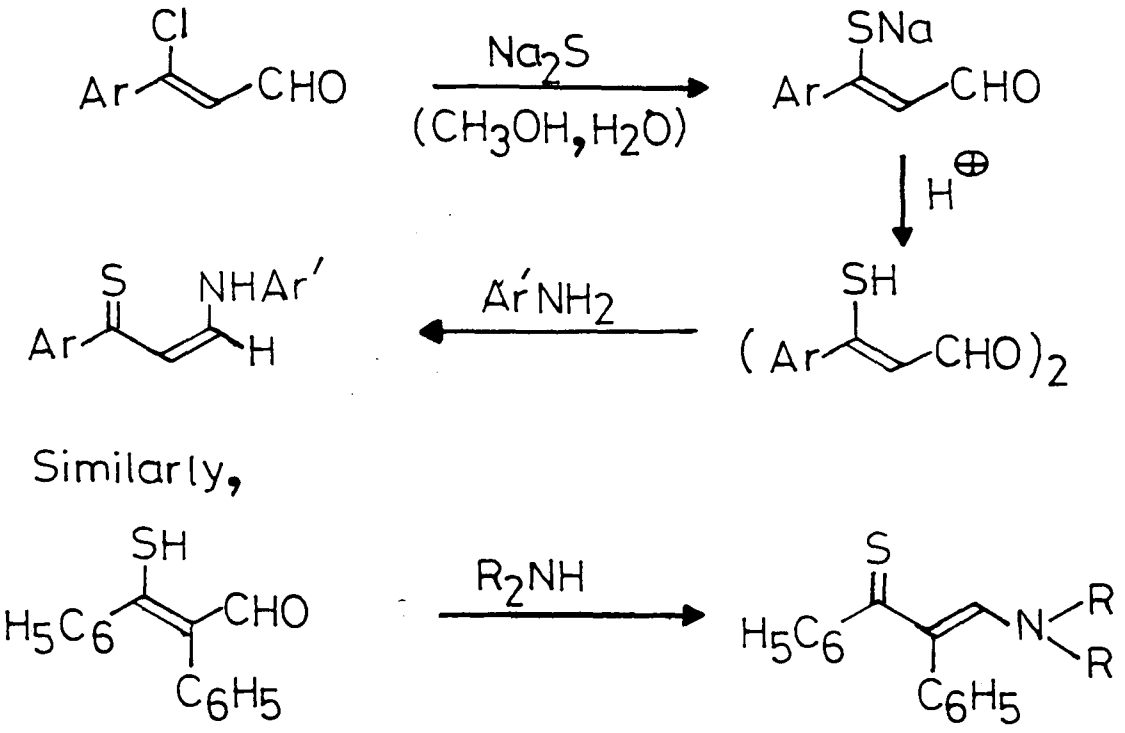
A careful scanning of literature reveals that almost all reported methods of synthesis of thioamide vinylogs are based on one of the following three approaches. The first approach involves the conversion of carbonyl or its O-alkylated derivative into a thiocarbonyl or of a carbon chloride into a thiol or thiolate. The sulfur is introduced in the last step and is provided by phosphorous sulphides, hydrogen sulphide, alkaline metal sulphides etc. The methods under this category are summarised in Scheme 1.

The second approach involves the reaction of an amine with ethylenic ß-mercapto-aldehydes where the mercapto group is attached before condensation of the amine on the aldehyde[15-17] (Scheme 2).

The third approach to the synthesis of thioamide vinylogs involves the opening of sulfur-containing rings (1,2-dithiole


Yield
Ref.
P4S10
(CS2)
50%
3-6
(p-H3COC6H4-PS2-)
20-74%
7
H2S
C2H5OH,HCl
less than
12%
6, 8
R=alkyl
Et3OBF4
CH2Cl2
HNaS
(abs.EtOH)
30-60%
9-11
Na2S
(DMF)
12-14

Scheme 1



Similarly,

Scheme 2

or isothiazole) which are usually of a cationic nature. The ring opening is effected by an amine or hydrogen sulfide (Scheme 3).

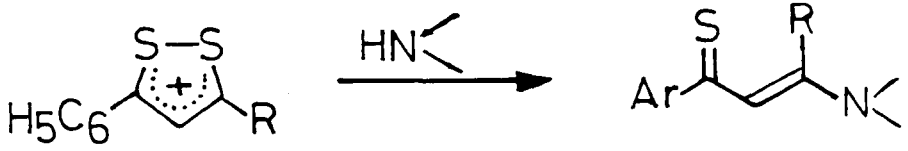
Reactions of thioamide Vinylogs:

The thioamide vinylogs are stable crystalline red compounds and form a group of extremely reactive synthons which undergo a number of addition elimination reactions. These also undergo a large variety of (4+1) and (4+2) cycloaddition reactions resulting in various heterocyclic compounds. The characteristic reactions of these thioamide vinylogs also include the electrophilic reactions at sulphur, nucleophilic reactions at carbon 1 and 3[28].

Electrophilic reactions at sulphur:

The thioamide vinylogs have been known to react readily with methyl iodide leading to S-methylated salt. For example, N,N-dialkylated thioamide vinylogs (2) on treatment with methyl iodide resulted in imminium salts (3) which can be hydrolysed to aldehyde (4) and in turn reduced to alcohol (5). The deprotonation of the imminium salts formed in case of N-aryl-thioamide vinylogs (6) resulted in a potential heterodiene, 1-aryl-1-aza-1,3-butadiene (7)[29,30] (Scheme 4).

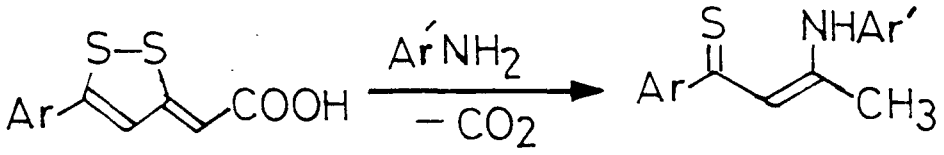
The similar imminium salt obtained on treatment of 2 with α-bromomethylketones could be cyclised to 2-acylthiophenes (8)[31]. Similarly when 2 was reacted with phenylacetyl chloride the resulting iminium chloride (9) on addition of triethylamine

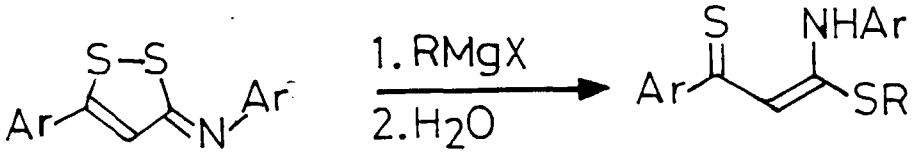
	Yield	Ref.
	upto 90%	5,8,9, 18-24

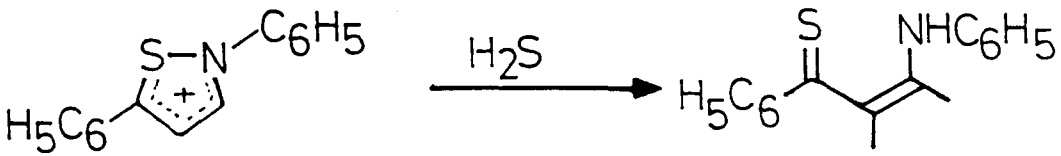
R=H, Ar

when R=Ar, two isomers are sometimes obtained which are difficult to separate. — 25

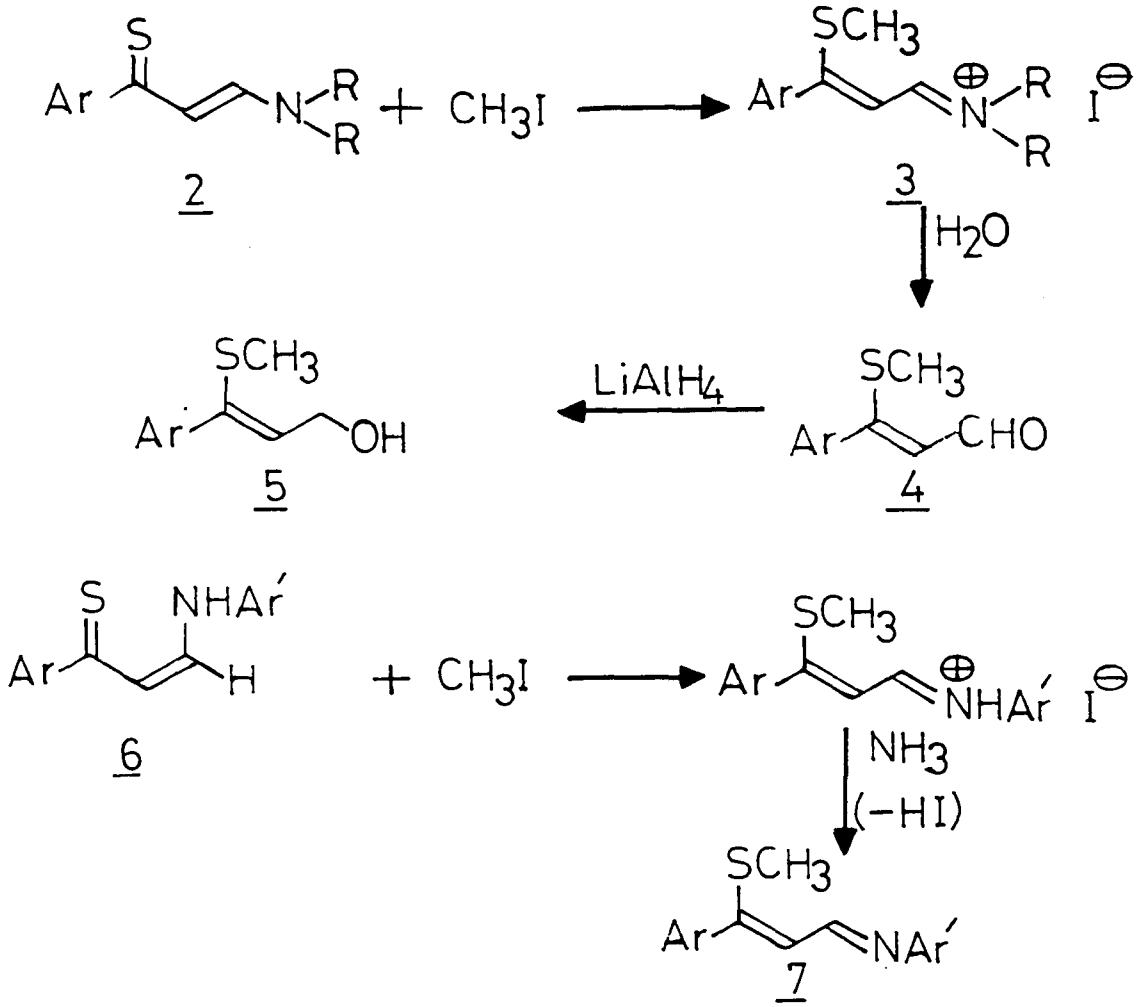
when $R=CH_3$, it leads to unexpected bimolecular condensation

 — 4

 — 26

 20-52% 27

Scheme 3


S
Ar
N
R
R
+ CH3I
SCH3
Ar
N
R
R
I
2
3
H2O
SCH3
Ar
OH
5
LiAlH4
SCH3
Ar
CHO
4
S
NHAr'
Ar
H
6
+ CH3I
SCH3
Ar
NHAr'
I
NH3
(-HI)
SCH3
Ar
NAr'
7

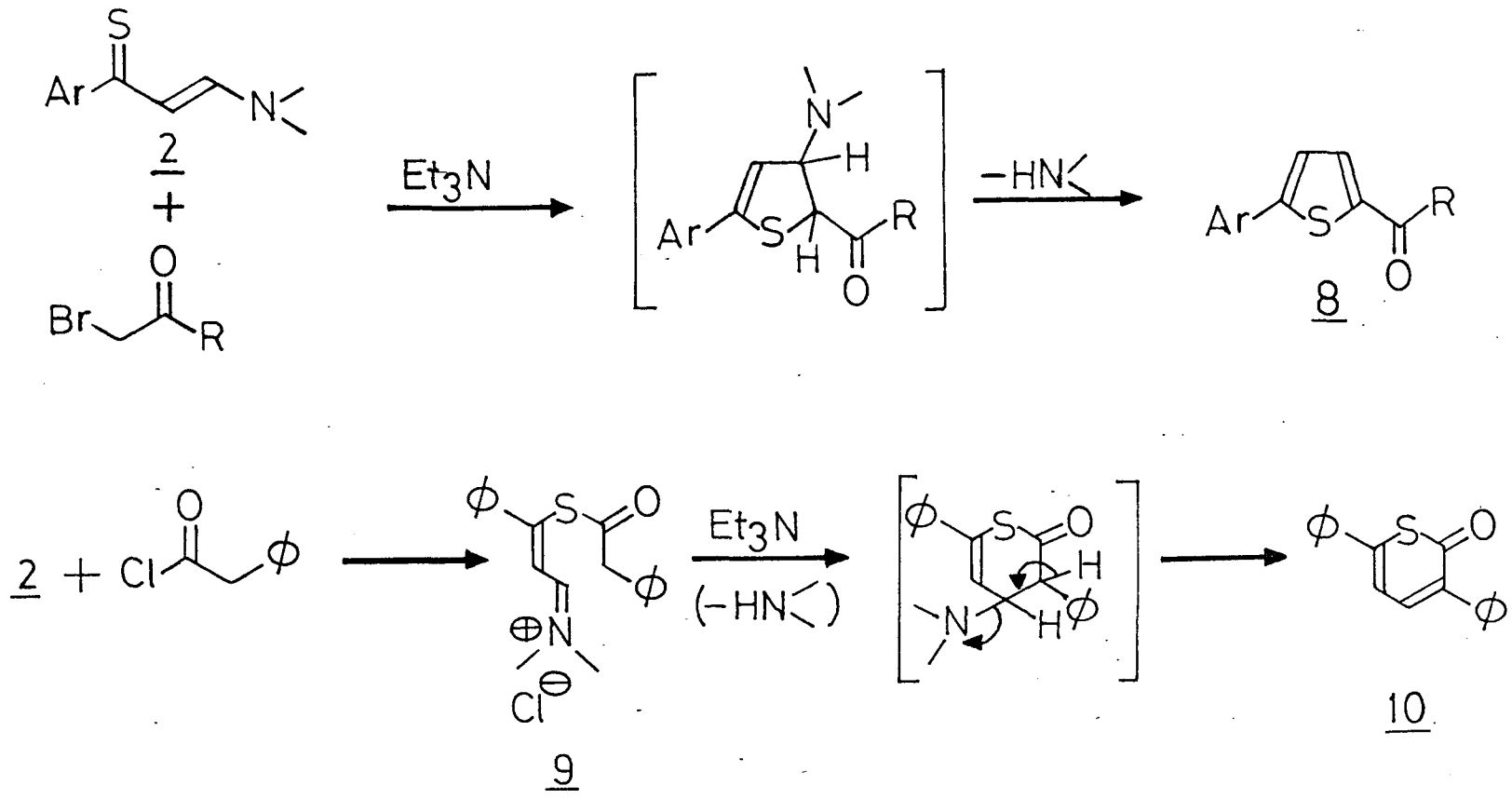
Scheme 4

underwent cyclisation to thiopyranone (10)[31]. This could be considered as a phenylketene equivalent reaction of thioamide vinylogs (2) (Scheme 5).

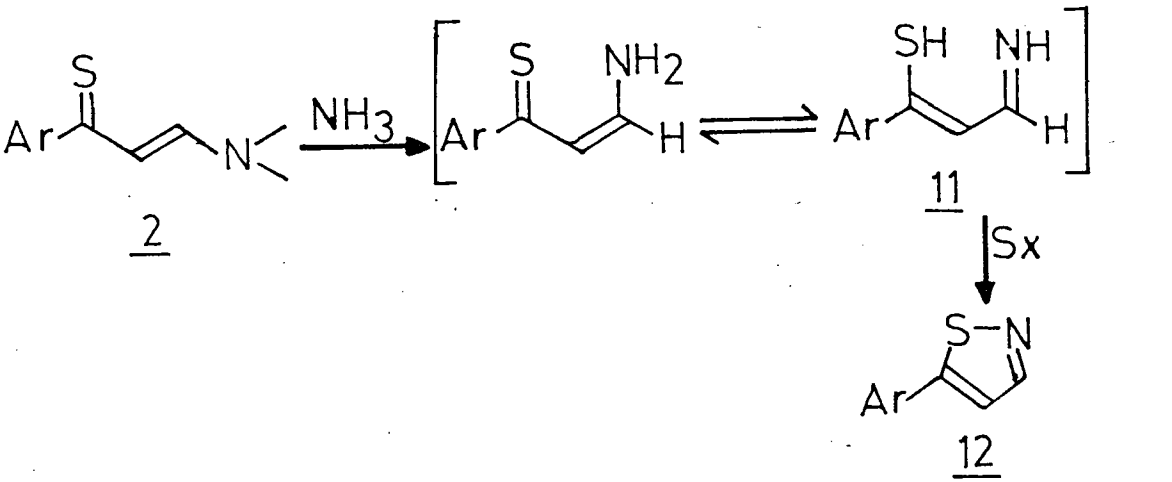
Nucleophilic reactions at carbons 1 and 3:

The thioamide vinylogs are known to undergo nucleophilic reactions at carbons 1 and 3 with a number of nucleophilic reagents. For example, isothiazoles (12) are isolated when the thioamide vinylogs (2) are reacted with ammonia in presence of elemental sulfur and the reaction was thought to proceed through the intermediate vinylog with no substituent at nitrogen (11)[30]. The intermediate vinylog could be isolated by the reaction of aqueous ammonia with the thioamide vinylog having identical substituents at carbon 1 and 3 (Scheme 6). The transamination of thioamide vinylogs is a very general reaction[32] (Scheme 7, Reactions 1-6). The alkylamine and arylamine groups could be substituted by other alkylamines and arylamines using amine acetate or amine hydrochloride in ethanol[32]. The attack of amines on the thiocarbonyl group could be realised by their reaction in presence of acetic acid and sodium acetate[33](Scheme 7). The thioamide vinylogs have also been known to react with hydroxylamine, hydroxylamine-O-sulphonic acid and with hydrazine to give isoxazoles[10], isothiazoles[34] and pyrazoles[30,35] respectively.

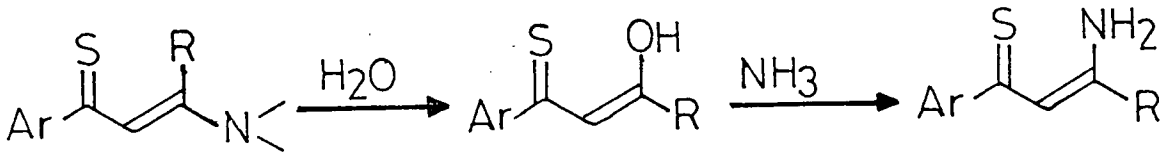
When the thioamide vinylogs are reacted with organomagnesium or organolithium compounds the nucleophilic attack at carbon 3



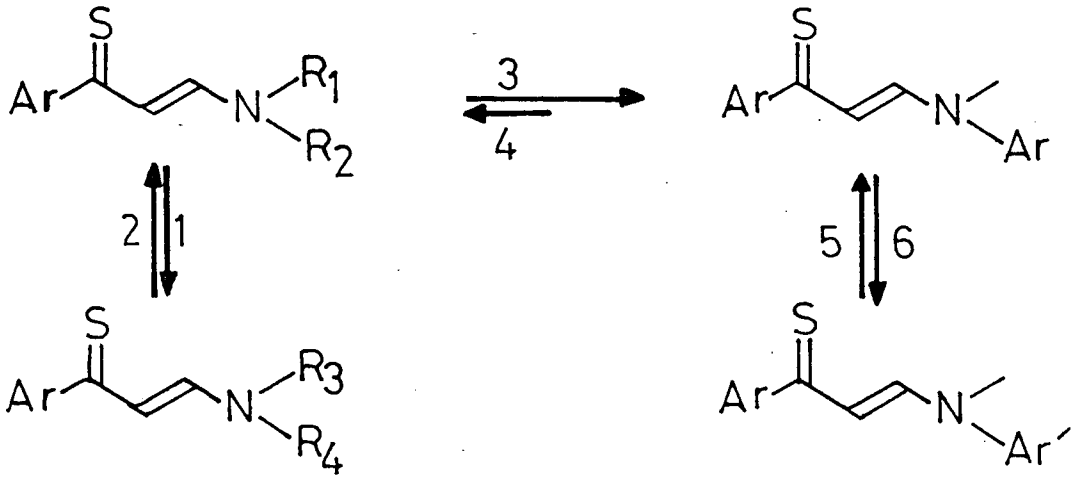
Scheme 5



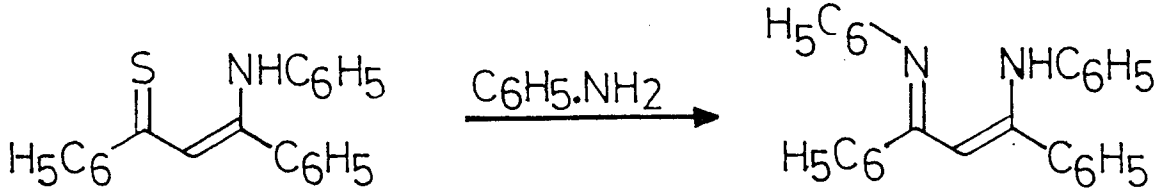
2 11 12



Scheme 6



R_1, R_2, R_3 and R_4 : aliphatic substituents



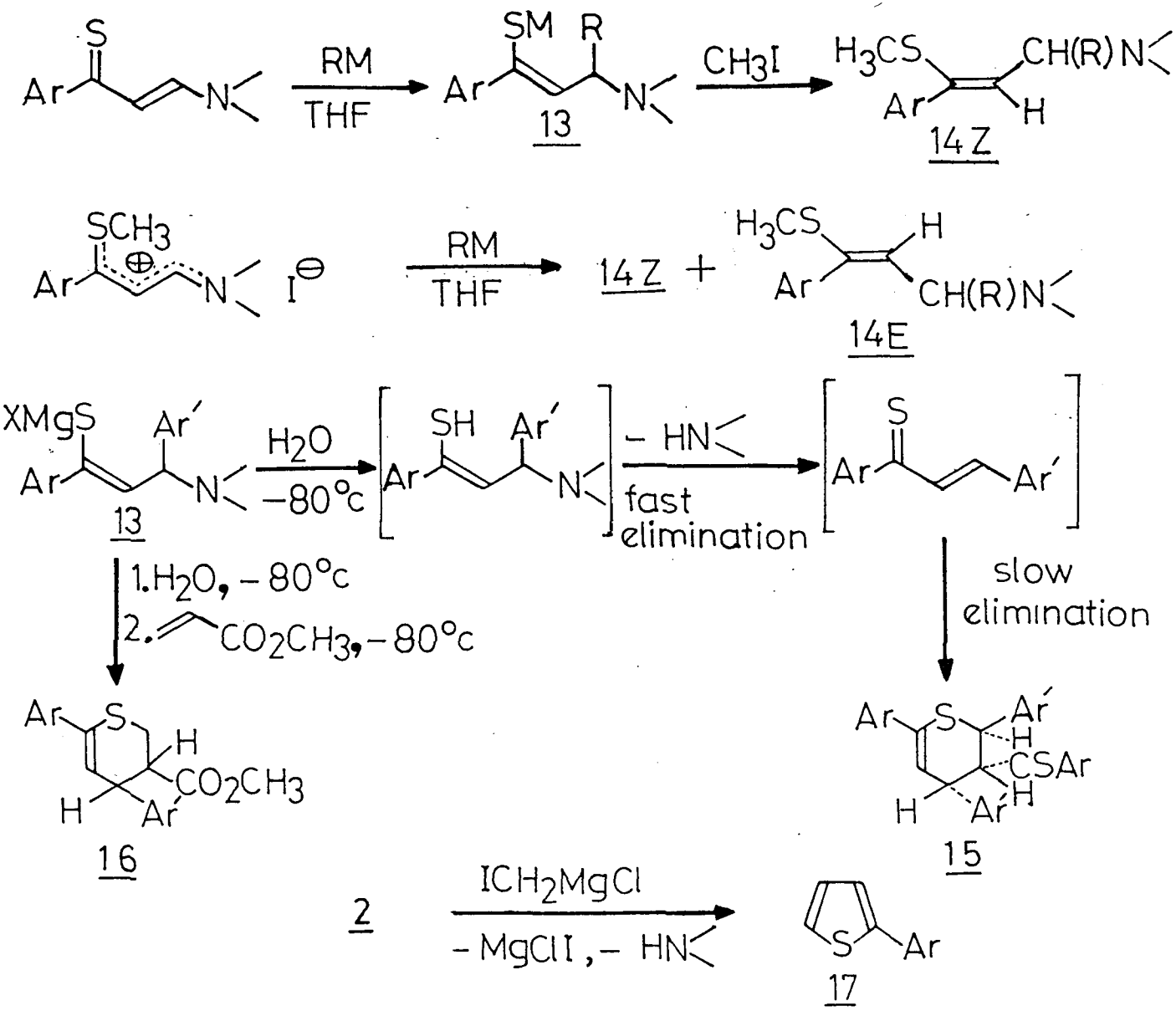
Scheme 7

of the vinylog at $0^{o}C$ (or at $-80^{o}C$) resulted in 1,4-addition reaction. Quiniou et al[36,37] have studied these reactions in detail and have made a number of interesting revealations. For example, when organomagnesium (or lithium) reagents were treated with thioamide vinylogs the initially formed metal complex on alkylation led exclusively to Z-α,β-unsaturated thioether(14). In contrast the inverse reaction of the iodomethylated thioamide vinylogs resulted in a mixture of Z and E isomers. Interestingly, the intermediate 13 obtained in the case of the addition of arylmagnesium halide to the thioamide vinylogs did not lead either to the aminated and possibly enethiolyzed thioketone, or its elimination product the ethylenic thioketone. The only compound isolated was the dimer of ethylenic thioketone 15. The intermediacy of the metal complex 13, in these reactions was proved by its reaction with another dienophile which gave $\sim$9% of 16 and $\sim$55% of 15 (Scheme 8). Compounds of the type 16 could also be obtained in excellent yields by heating the dimer 15 in presence of acrylic compounds.

The treatment of the thioamide vinylogs 2 with iodomethyl-magnesium chloride gave the thiophene derivative 17 and is one of the rare examples of (1+4) cycloaddition reactions of metal carbenoids.

Cycloaddition reactions:

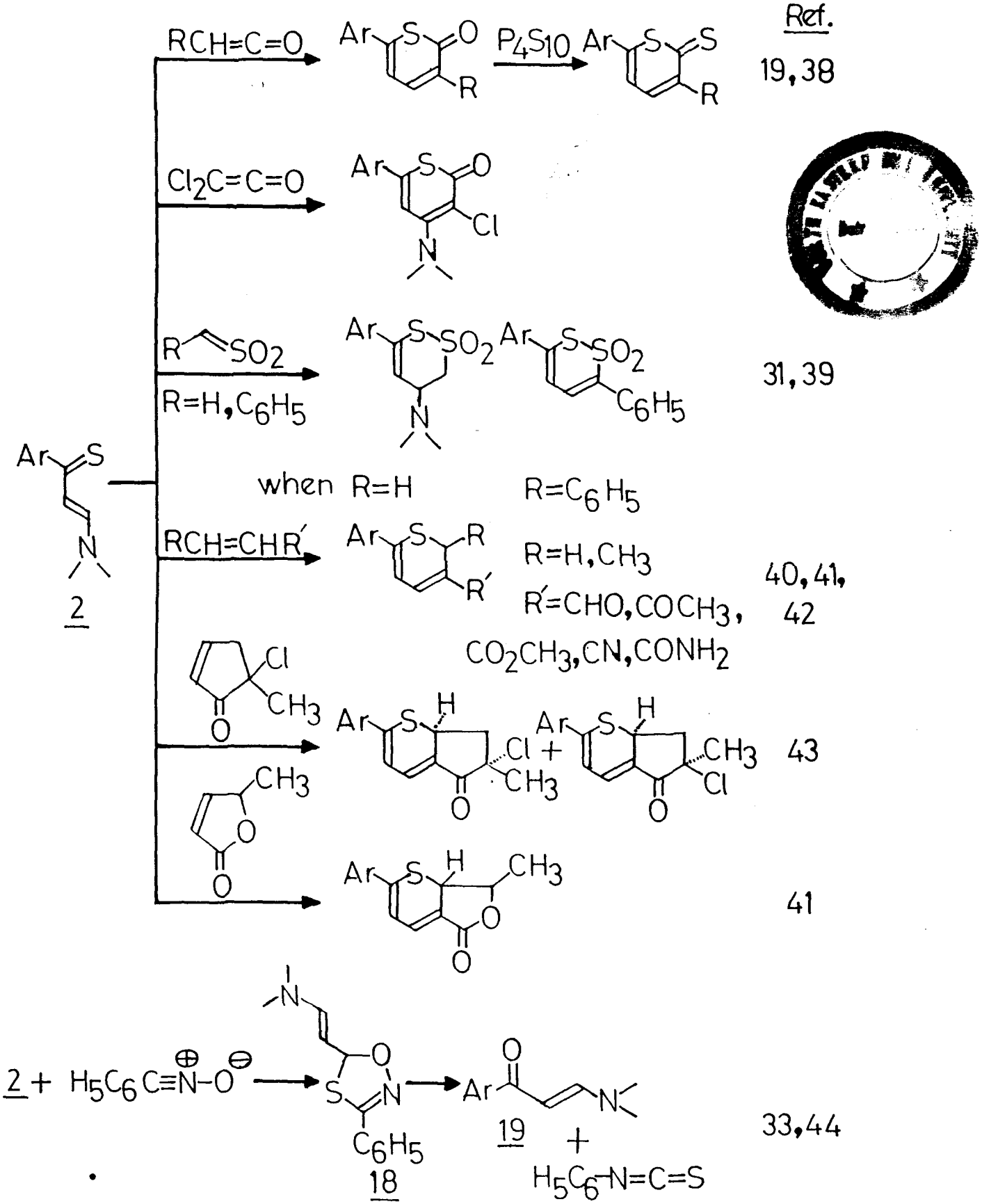
Thioamide vinylogs have been shown to behave as excellent hetero-dienes resulting in innumerable thiopyran derivatives with various


RM
THF
CH3I
13
14Z
14E
H2O
−80°C
fast elimination
slow elimination
1.H2O, −80°C
2. CO2CH3, −80°C
16
15
ICH2MgCl
− MgClI, − HN
17

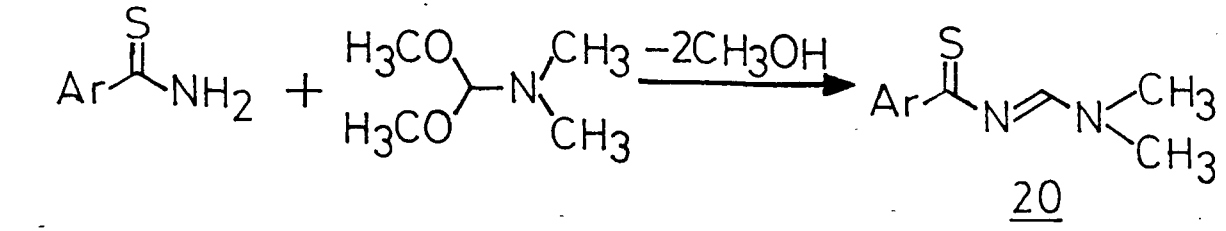
Scheme 8

dienophiles. Diels-Alder cycloaddition reactions of 2 with dienophiles like ketenes, sulphenes, aldehydes, ketones, esters, nitriles, acrylic amides and carbocyclic/heterocyclic compounds possessing an endocyclic double bond are summarised in Scheme 9. The reaction of thioamide vinylog with 1,3-dipolar benzonitrile oxide resulted in the conversion of thioamide vinylog to its oxygen analog. The reaction was believed to proceed through the oxathiazole intermediate (18) which decomposed to amide vinylog (19)[33,34].

N,N-dimethyl-N'-thioaroyl formamidines (20), a structural analog of thioamide vinylog where the carbon adjacent to thiocarbonyl is replaced by a nitrogen atom, constitute another group of extremely reactive synthons which leads to the synthesis of a large variety of heterocyclic compounds. The thioaroylformamidines (20) formed easily by the reaction of thioamides with N,N-dimethylformamide dimethylacetal[45] have been found to decompose to starting thioamide on exposure to moisture. Lin et al have reported that the reaction of N'-thioaroyl-N,N-dimethylformamidines (20) and N'-phenylthiocarbamoyl-N,N-dimethylformamidines[46] (21) with an aminating agent such as O-(mesitylenesulfonyl) hydroxylamine[47] or hydroxylamine-O-sulfonic acid[46] led to the formation of 1,2,4-thiadiazoles (22) (Scheme 10). Quiniou et al have shown that thioacylformamidines like thioamide vinylogs, undergo successful (4+2) cycloaddition reactions with ketenes, sulfenes, α,β-unsaturated ketones, α,β-unsaturated


Ref.
RCH=C=O
P4S10
19,38
Cl2C=C=O
R=SO2
R=H,C6H5
31,39
when R=H
R=C6H5
RCH=CHR'
R=H,CH3
R'=CHO,COCH3,
CO2CH3,CN,CONH2
40,41,
42
2
43
41
2 + H5C6C≡N-O
18
19
+
H5C6-N=C=S
33,44

Scheme 9



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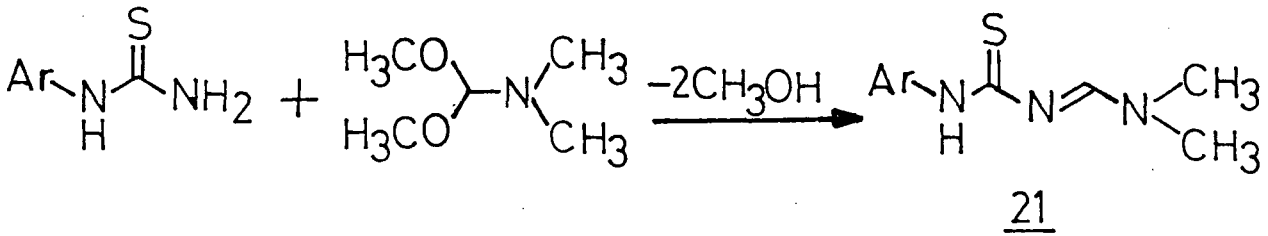

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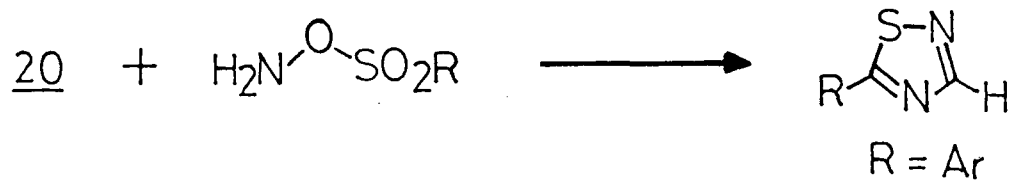
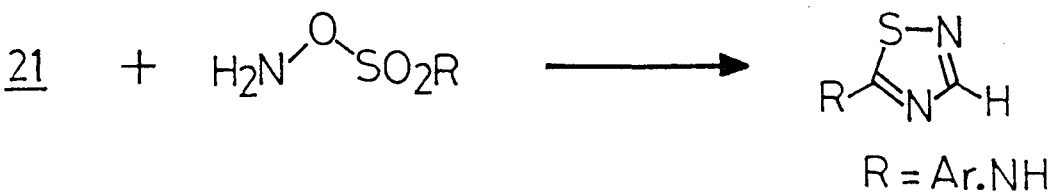


R = Ar



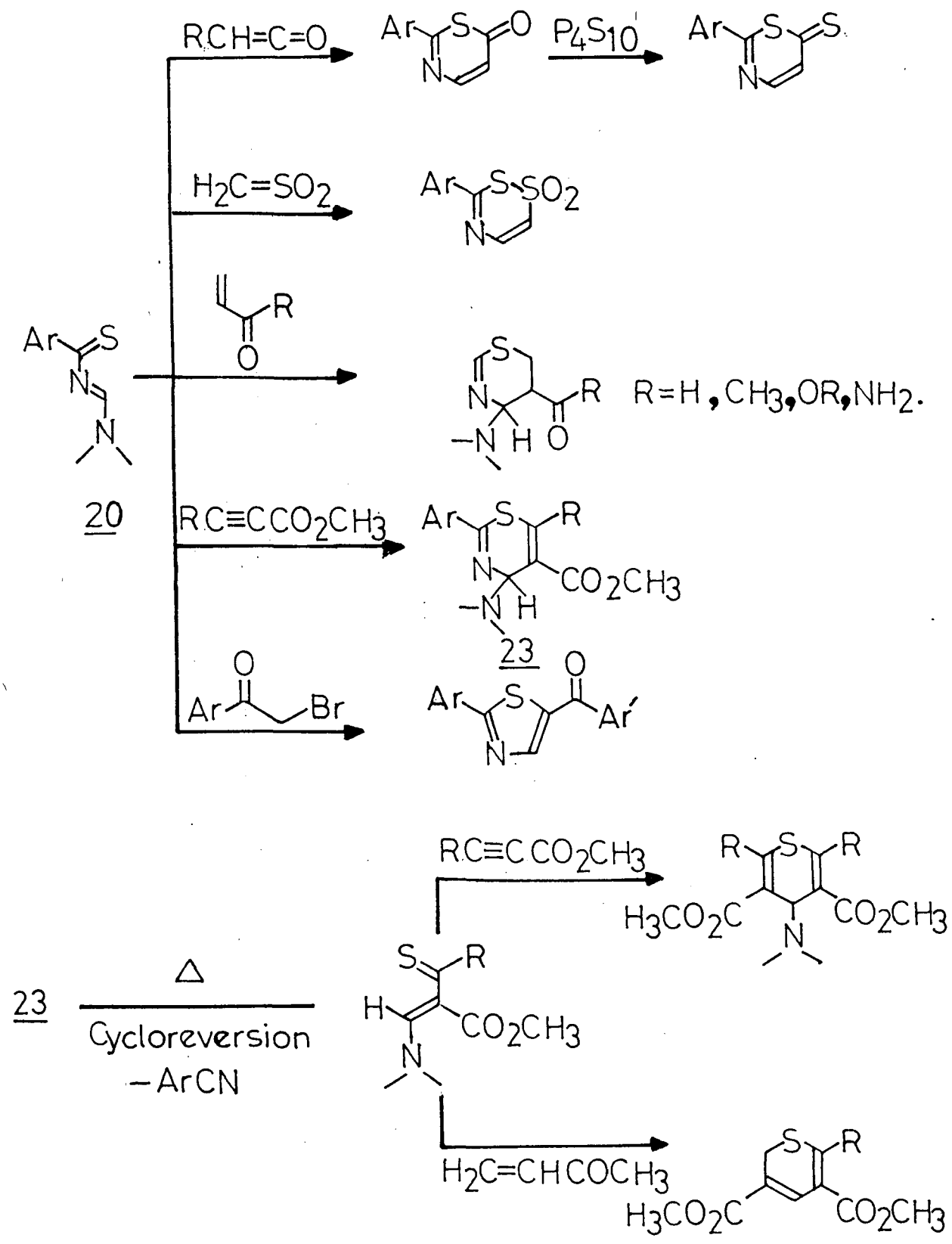
R = Ar.NH

22

Scheme 10

esters, α,β-unsaturated nitriles, and α,β-unsaturated amides resulting in various thiazines derivatives. Thioacylformamidines (20) were also found to react with α-haloketones to give thiazole derivative[48-50] (Scheme 11). Quiniou et al have reported that the cycloadducts 23, formed in the case of the reactions of thioacylformamidines with acetylenic esters undergo retero Diels-Alder reactions resulting in new thioamide vinylogs which in turn reacted with different dienophiles to yield various thiopyran derivatives[51]. It has been established that the presence of electron donating substituents ($\dot{N}<$) at C-3 position of thioamide vinylogs stabilizes the monomeric forms and discourages the (4+2) dimerization reaction which normally occurs in other 1-thiabutadienes[52]. It also improves the 4π participation of thioamide vinylogs in Diels-Alder reactions with typical electron deficient dienophiles.

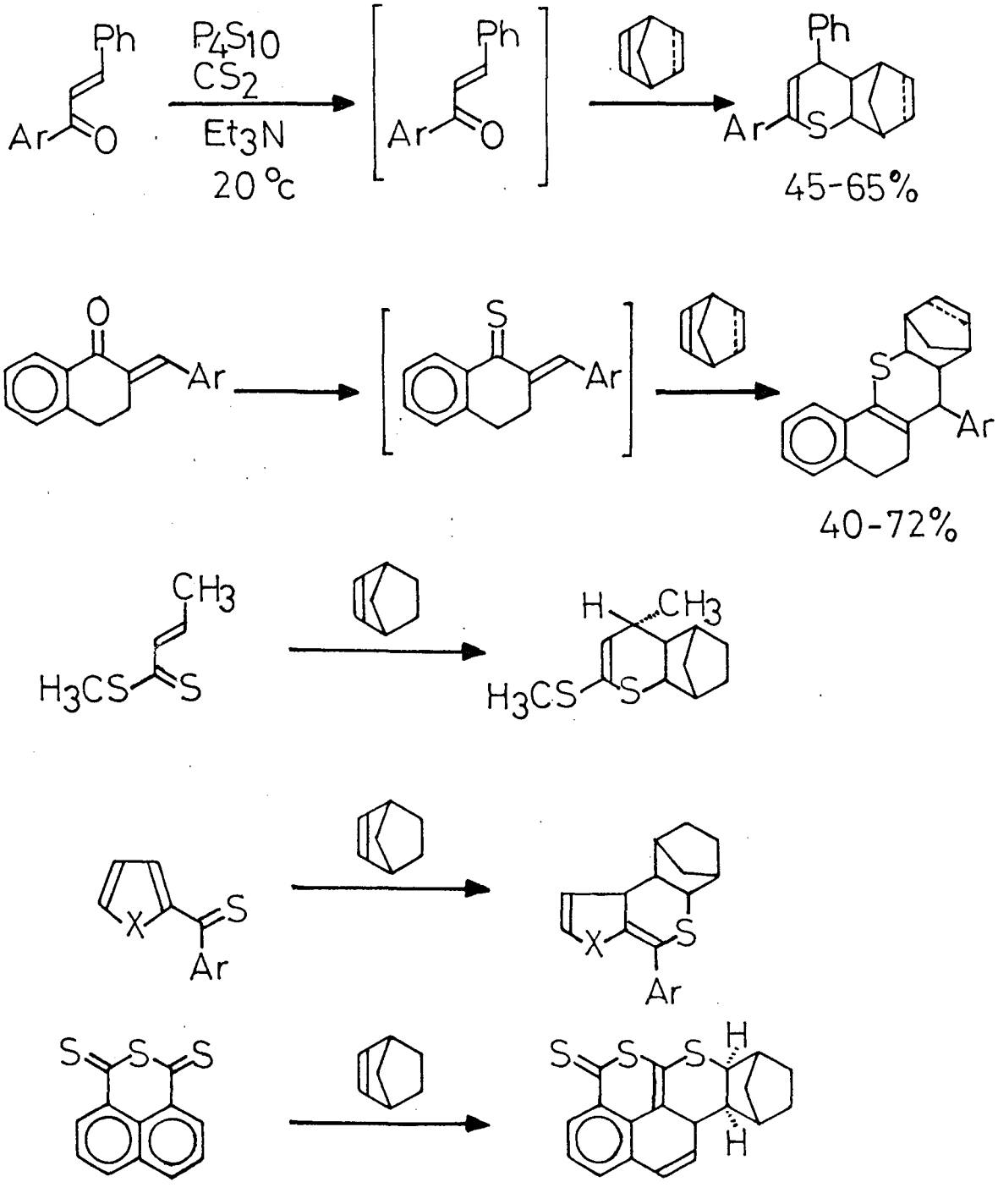
The literature survey clearly reveals that although there are a number of reports concerning the reactions of thioamide vinylogs and related compounds with electrophiles, nucleophiles and carbon-carbon dienophiles. The synthetic potential of these compounds still remain unexploited to a considerable extent. For example there are no reports concerning the reactions of these compounds with heterodienophiles, strained alkenes and other potential heterodienes. Hence it was considered worthwhile to investigate these aspects of thioamide vinylogs and related compounds.


RCH=C=O
P4S10
H2C=SO2
R
R=H, CH3, OR, NH2.
20
RC≡CCO2CH3
23
Ar
Br
Ar'
RC≡C CO2CH3
H2C=CHCOCH3
H3CO2C
CO2CH3
Δ
Cycloreversion
−ArCN

Scheme 11

The azodicarbonyl compounds have been found to participate both as 4π and 2π components in the Diels-Alder cycloaddition reactions with dienophiles and dienes. However their behaviour towards other potential heterodienes have not been investigated. With a view to establish the high reactivity of thioamide vinylogs as heterodienes towards azo carbonyl compounds, the investigations concerning the reactions of thioamide vinylogs with ethyl azodicarboxylate are reported in chapter II. The various substituted thiadiazines resulting from these reactions are characterized on the basis of analytical and spectral data. The stereochemistry at C-4 in these thidiazines is clearly defined on the basis of coupling constants JH_4H_5.

The nitroalkenes, in general, participates as a 2π component in Diels-Alder reactions with all carbon dienes[53,54]. It has also been found to participate as 4π component in case of reactions with alkenes, enol ethers, enolates, allylsilanes and enamines[55-62]. Also, Gilchrist and co-workers have shown that the nitrosoalkenes participate as 2π and 4π components in case of reactions with all carbondienes and dienophiles respectively. We have investigated the reactions of nitroalkenes and nitrosoalkenes with enamino-thiones in order to understand as to which of these components behaves as a diene and which as a dienophile. The results of these investigations are reported in chapter III. In case of nitroalkenes the



Scheme 12

products, thiopyran derivatives are characterized on the basis of analytical and spectral data. The stereochemistry at the individual carbon atoms is defined on the basis of coupling constants. In case of nitrosoalkenes the products have been characterized as 3-aryl-3-(2-aryl-2-oximinoethylthio) prop-2-enal.

There have been few reports of formal 4π participation of 1-thiabutadienes with strained alkenes such as norbornylene[63-66] (Scheme 12). We have investigated the 4π participation of thioamide vinylogs with norbornylene and dicyclopentadiene which also form part of chapter III.

The chapter IV deals with the reactions of thioamide vinylogs with isonitriles and isothiocyanates. This chapter also includes the reactions of N,N-dimethyl-N'-thiobenzoylformamidine and N,N-dimethyl-N'-phenylthiocarbamoylformamidine with N-aryl-benzimidoyl chlorides. The probable mechanistic pathways leading to the formation of various products in these reactions have also been discussed.

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CHAPTER II

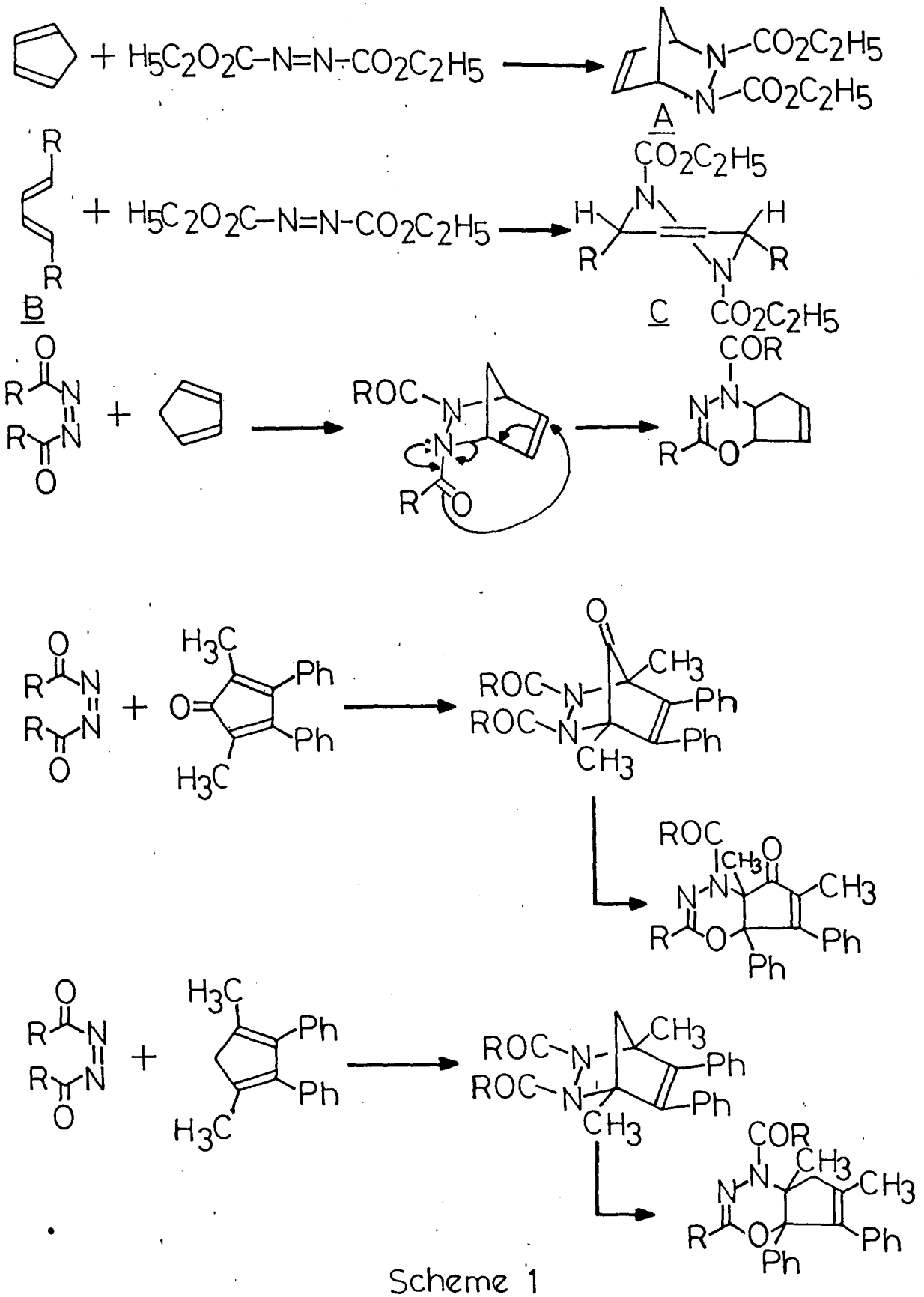
CYCLOADDITION REACTIONS OF THIOAMIDE VINYLOGS WITH ETHYL AZODICARBOXYLATE

2.1 INTRODUCTION

In general, the -N=N- dienophiles are more reactive than the corresponding -C=C- compounds, because of their low energy LUMO. Azo compounds in which the azo bond is flanked by one or two carbonyl groups, in contrast to the aliphatic or aromatic azo compounds, possess a highly reactive -N=N- bond which readily participates in cyclo-addition reactions. In recent years the azo compounds

flanked by carbonyl groups have found wide use as reactive dienes, dienophiles, enophiles and electrophiles. Many of these reactions easily lead to a variety of heterocyclic compounds. Some of these aspects concerning azo carbonyl compounds are summarised in recent reviews[1,2].

The first use of diethyl azodicarboxylate as a dienophile was reported in the formation of Diels-Alder adduct A with cyclopentadiene[3]. The Diels-Alder reactions of diethyl azodicarboxylate and 4-substituted butadienes B occur rapidly, and the adducts C are obtained in high yield wherein the initial configuration of the diene substituents is retained[4]. It has also been reported that in certain cases the initial Diels-Alder adducts of azodicarbonyl compounds are labile and undergo rearrangements. In a series of articles Mackay et al[5] have shown the initial Diels-Alder adducts the diazines formed by the reactions of cyclopentadiene, cyclopentadienones and 2,5-dimethyl-3,4-diphenyl cyclopentadiene with azodicarboxylates rearrange to 1,3,4-oxadiazines the formal Diels-Alder adducts formed by 4π participation of azodicarbonyl compounds (Scheme 1). In a recent review article D.L. Boger has discussed that azodicarboxylates are best recognised, for their ability to participate as 2π components in Diels-Alder reactions with dienes and for their effective participation in the reactions with simple olefines[2]. However olefines which do not



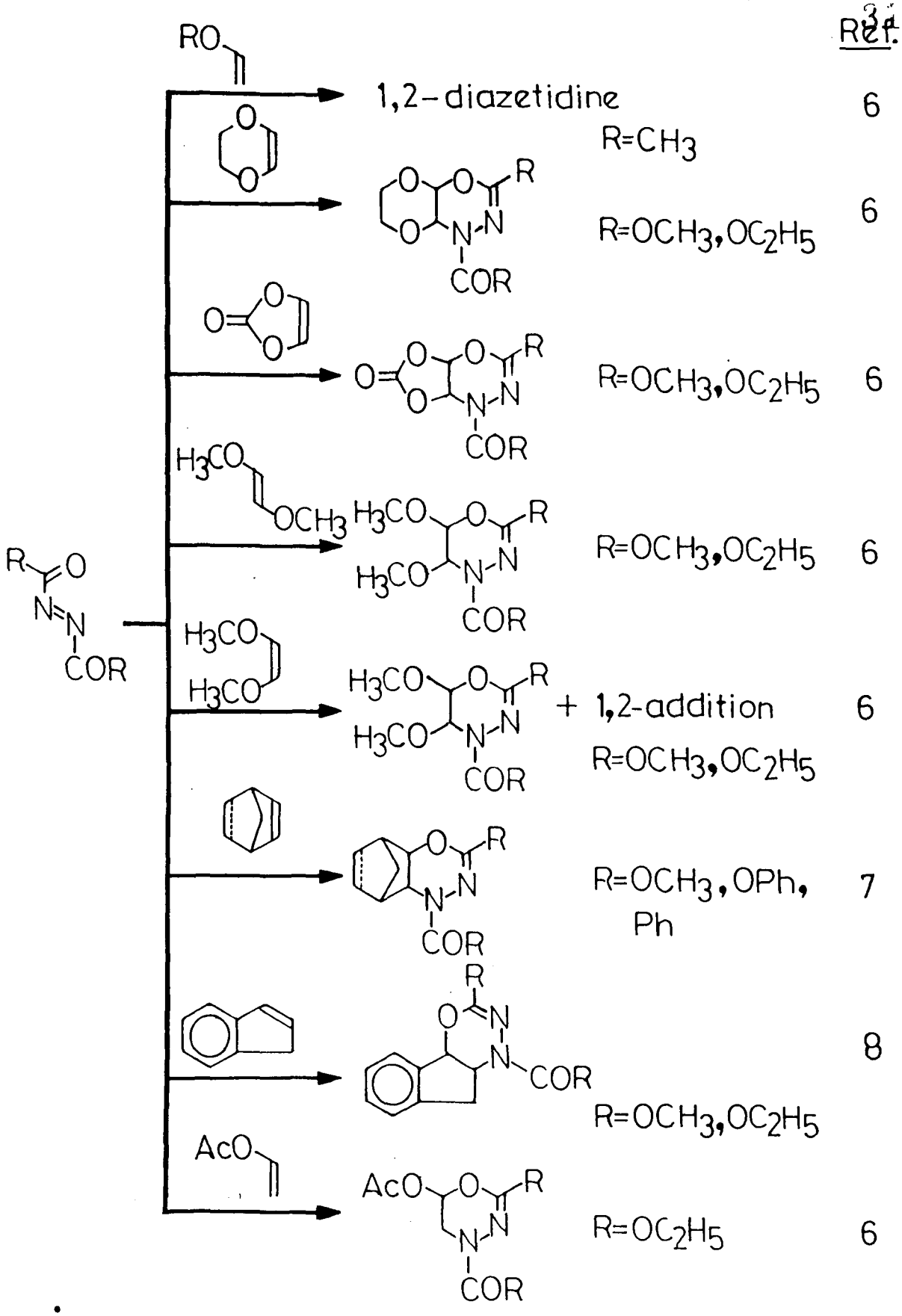
Scheme 1

contain a reactive allylic hydrogen and therefore cannot enter into an ene reaction may react with azo dicarbonyl compounds by two different modes: (2+2) cycloaddition to give 1,2-diazetidines and (4+2) cycloaddition to give 1,3,4-oxadiazines with the azo dicarboxylate acting as 4π component of the cycloaddition. Typical 4π Diels-Alder reactions are summarised in Scheme 2[6-11].

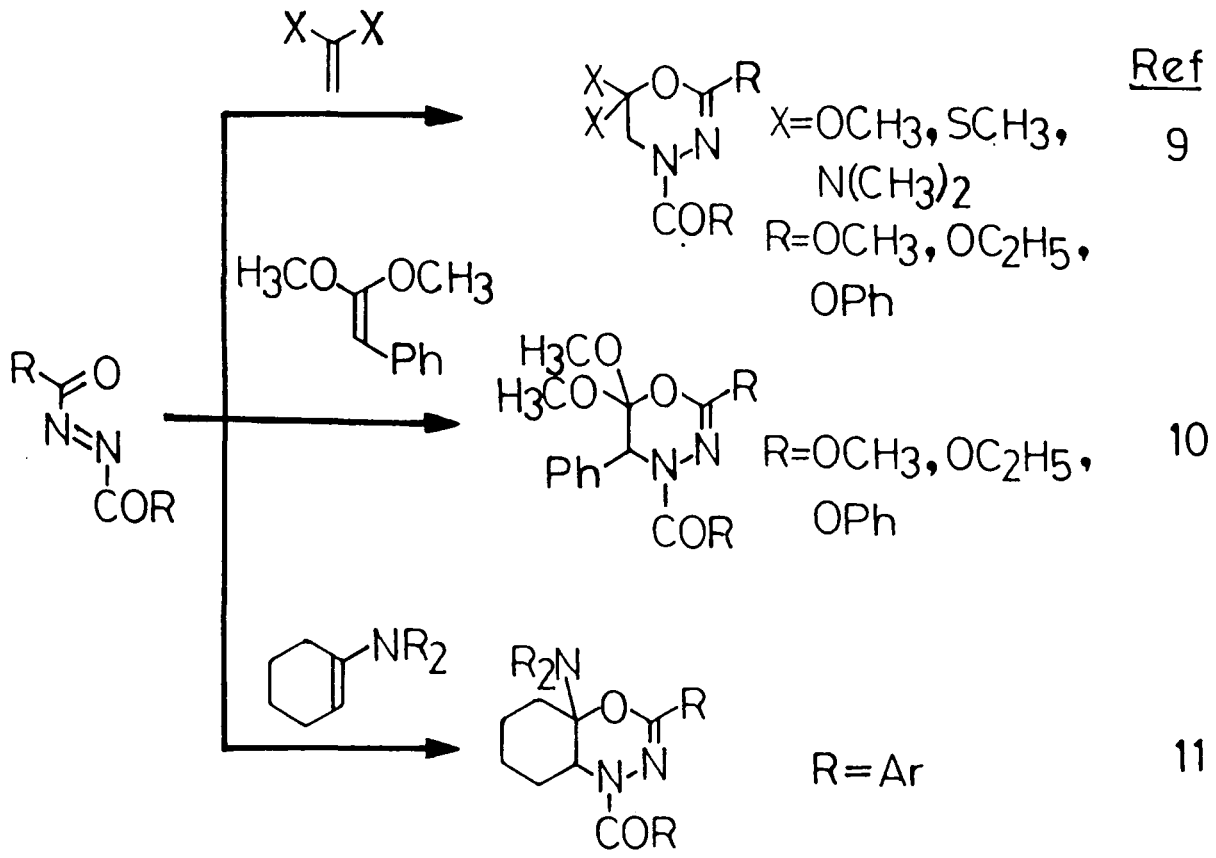
Apparently a number of reports have appeared in literature concerning the reactions of azo carbonyl compounds with electron rich olefines and all carbon dienes but the reports concerning reactions of azo carbonyl compounds and heterodienes are very rare. We have investigated the reactions of thioamide vinylogs with ethyl azodicarboxylate in order to examine the reaction pathway followed and the nature of the products formed in these cases.

2.2 RESULTS AND DISCUSSIONS

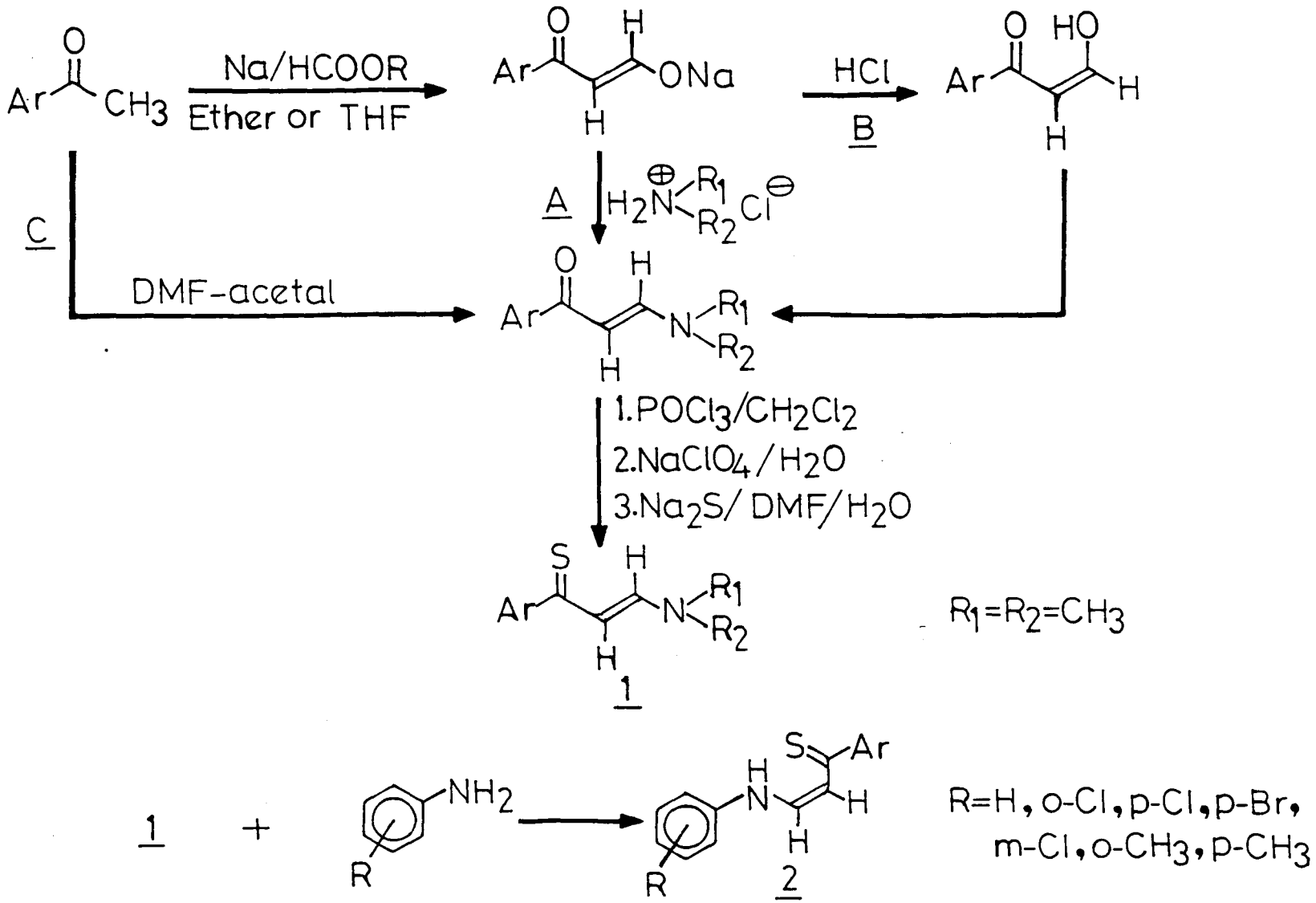
For the present studies the thioamide vinylogs have been prepared from enaminones (Scheme 3). A number of methods have been reported in literature[12-15] (Routes A and B) for the preparation of these enaminones and almost all of these have been used with varying degrees of success. For our purposes we have followed the method described in Route C[16-18] which have been found to give the best results. The enaminones are then converted to enaminothiones



Scheme 2 (contd.)


X=OCH3, SCH3, N(CH3)2
R=OCH3, OC2H5, OPh
R=OCH3, OC2H5, OPh
R=Ar
Ref
9
10
11

Scheme 2

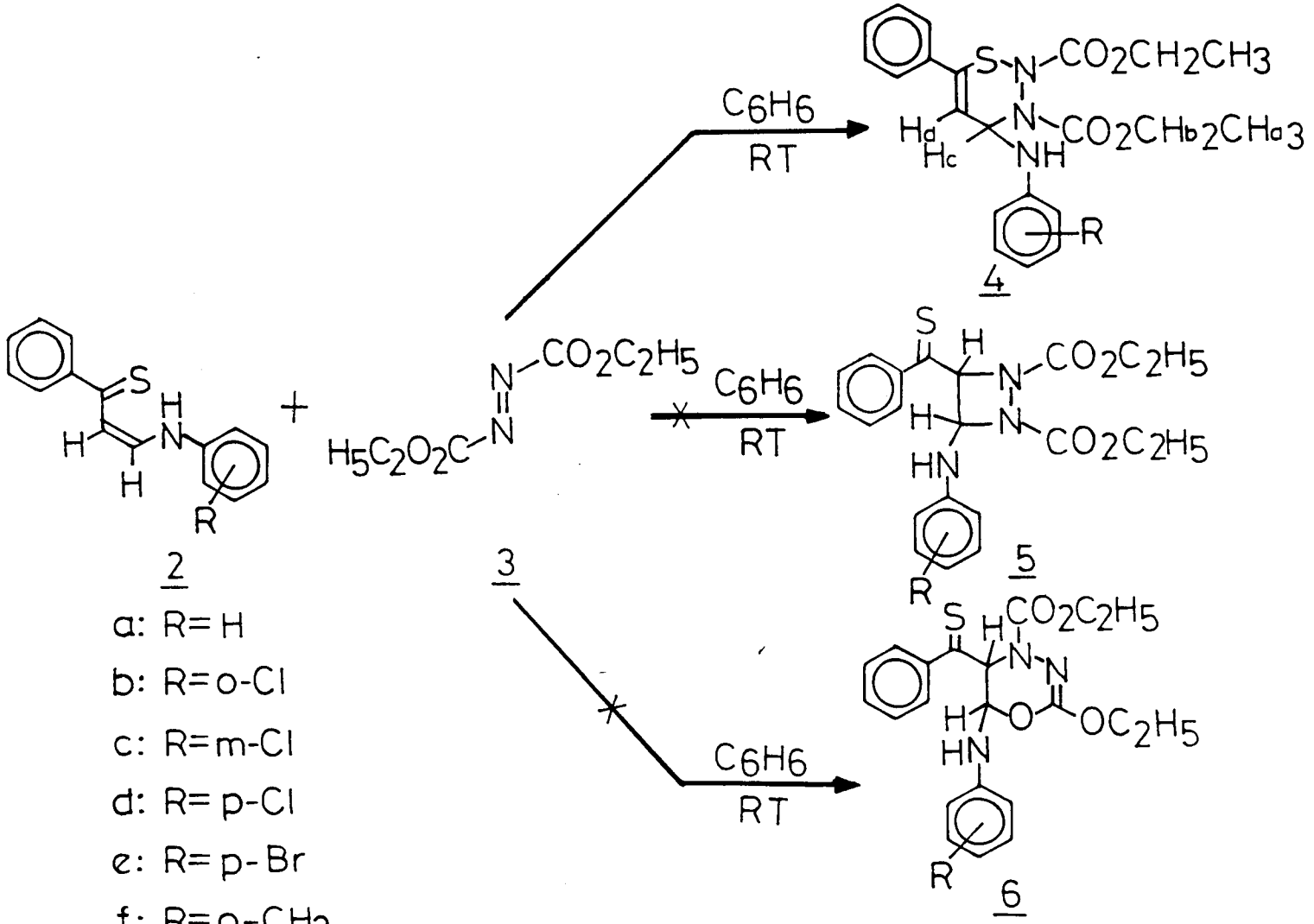

Na/HCOOR
Ether or THF
HCl
B
A
C
DMF-acetal
1.POCl3/CH2Cl2
2.NaClO4/H2O
3.Na2S/ DMF/H2O
R1=R2=CH3
1
2
R=H, o-Cl, p-Cl, p-Br,
m-Cl, o-CH3, p-CH3

Scheme 3

by the methods described in Scheme 3[19,20].

Treatment of 3-N-arylamino-1-phenylpropene-1-thione(2) with an equivalent amount of ethyl azodicarboxylate (3) in dry benzene followed by careful work-up of the reaction mixture resulted in very good yields (70-90%) of (4+2) cycloadducts which have been characterized as hitherto unknown 2,3-diethoxycarbonyl-4-N-arylamino-6-phenyl-4H-1,2,3-thiadiazines (4). The other possible structures, diazetidine derivatives 5 and oxadiazine derivatives 6 formed via the (2+2) cycloaddition of 2 and 3 and (4+2) cycloaddition of 2 and 3 involving 3 as 4π component respectively are ruled out on the basis of ^{1}H NMR and ^{13}C NMR spectra of the adducts.

Analytical results for compound 4a, for example, have shown that it has molecular formula $C_{21}H_{23}N_3O_4S$ and its IR spectrum showed a NH stretching frequency at 3375 cm^{-1} and the carbonyl absorption bands at 1730 and 1715 cm^{-1}. The proton NMR spectra of 4 are of interest, for example, ^{1}H NMR spectrum ($CDCl_3$) of 4a (Fig.1) showed two triplets at δ 0.83(3H) and δ 1.33(3H), a multiplet at δ 4.04(2H), another multiplet at δ 4.36(3H), a doublet at δ 6.00 (J=6Hz) (1H), a multiplet centred around δ 6.24, a doublet at δ 6.74(J=8Hz) and a group of partially resolved signals at δ 7.30(8H). Of the two triplets due to two methyl groups, the methyl group marked 'a' appears at



2

a: R= H

b: R= o-Cl

c: R= m-Cl

d: R= p-Cl

e: R= p-Br

f: R= o-CH_3

g: R= p-CH_3

3

4

5

6

Scheme 4

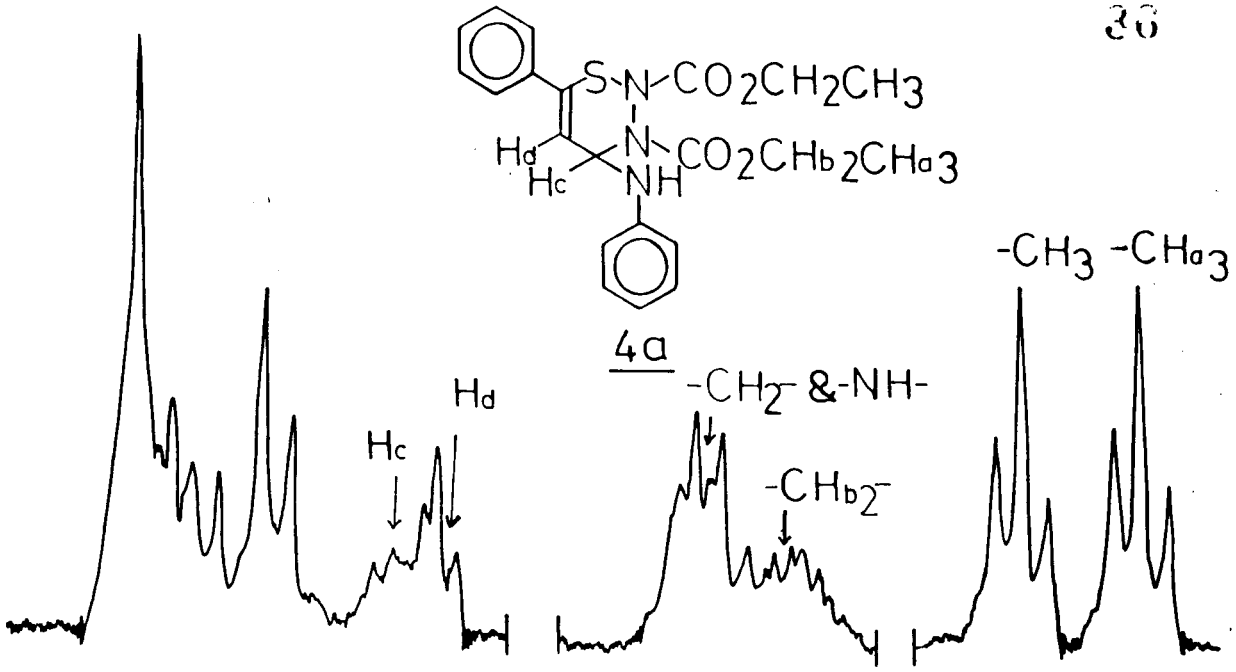


Fig. 1(in $CDCl_3$)

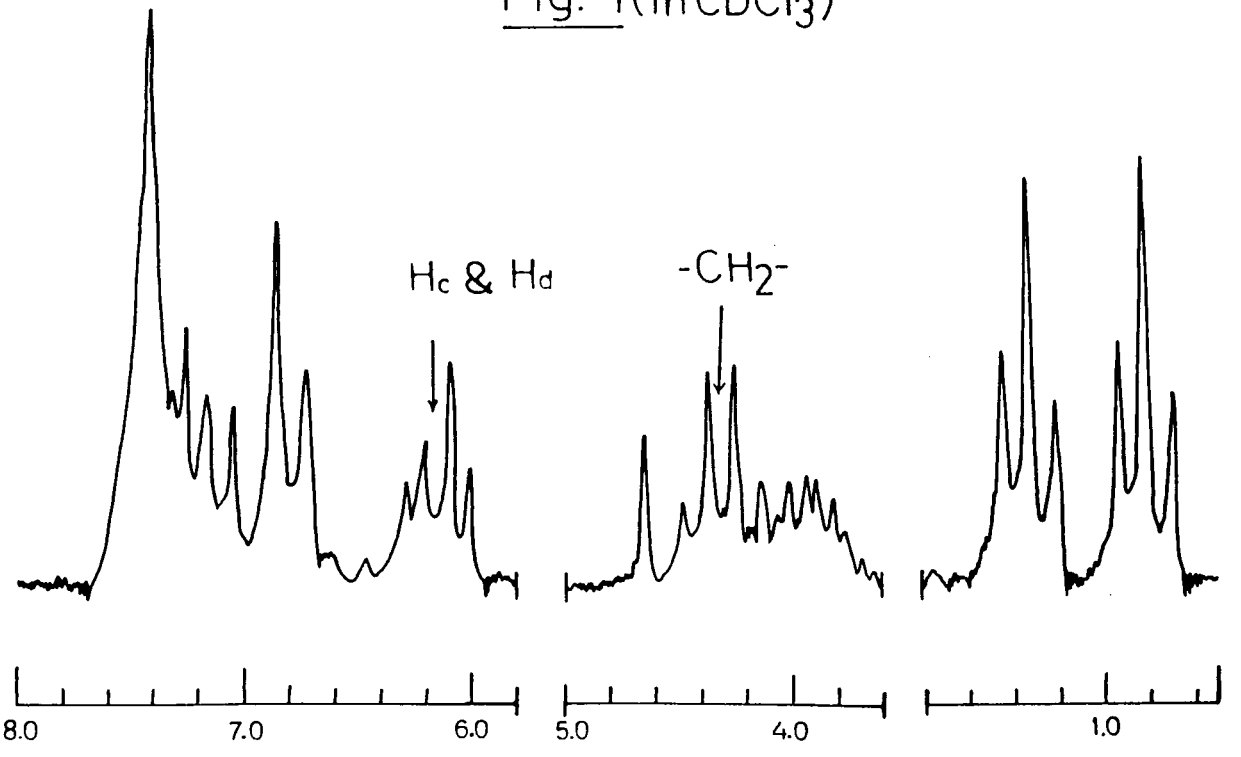


Fig. 2 (in $CDCl_3$ & D_2O)

^1H nmr Spectrum (60MHz) of 4a

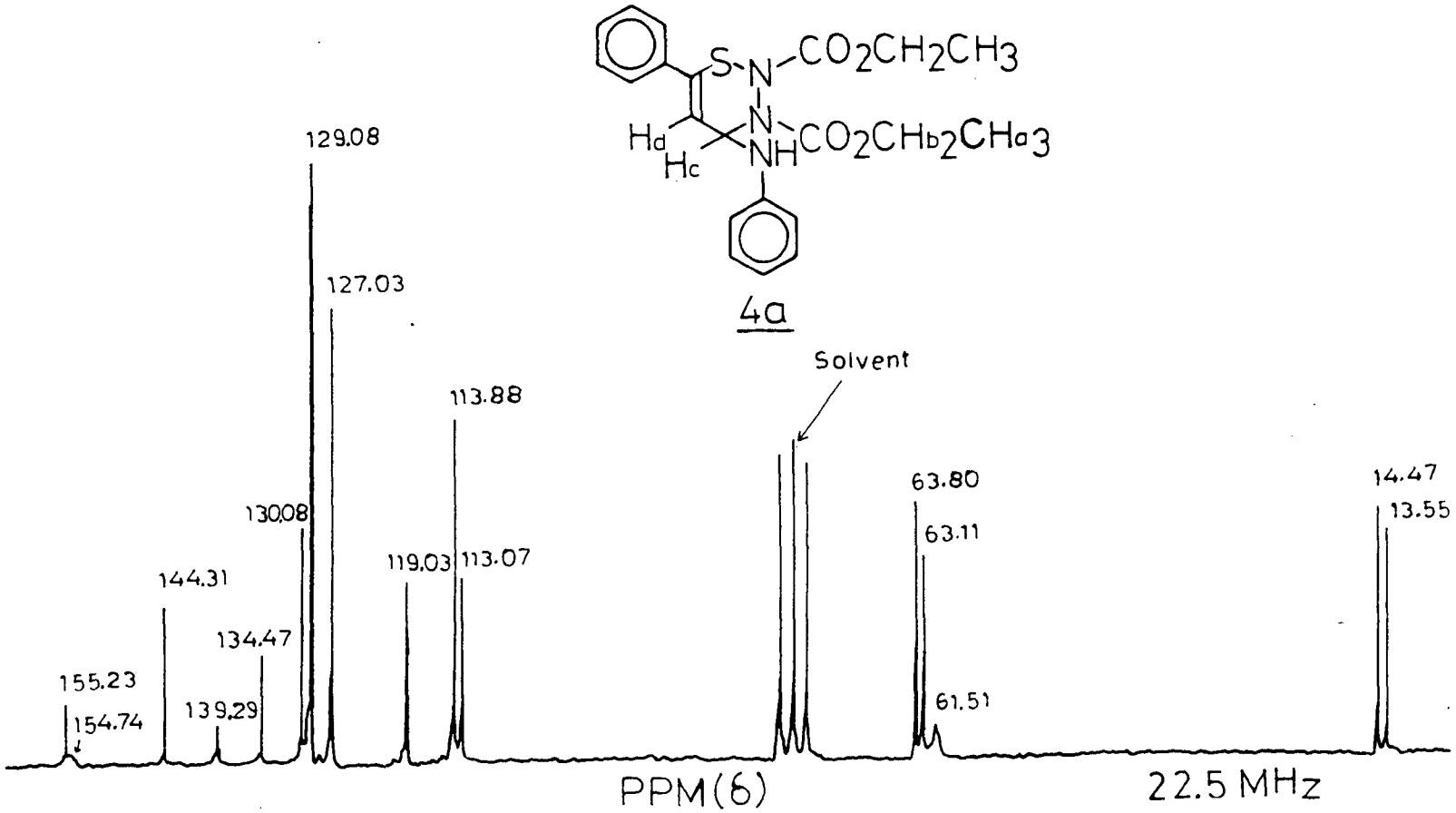


Fig. 3 (in $CDCl_3$)

^{13}C nmr Spetrum (decoupled) of 4a

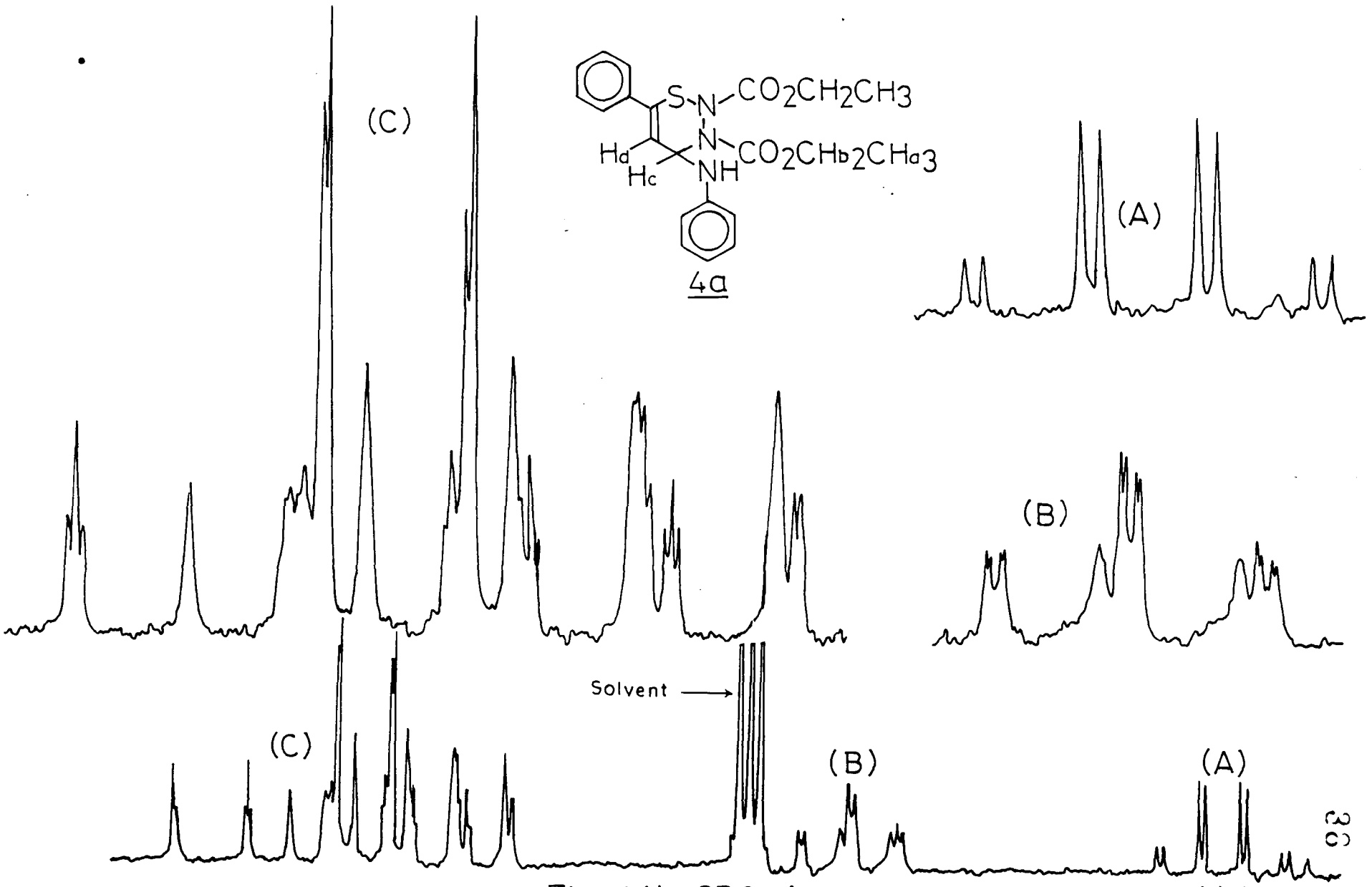
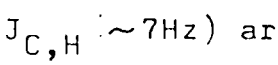
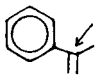
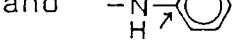
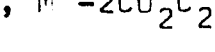


Fig. 4 (in $CDCl_3$)

^{13}C nmr Spectrum (coupled) of 4a

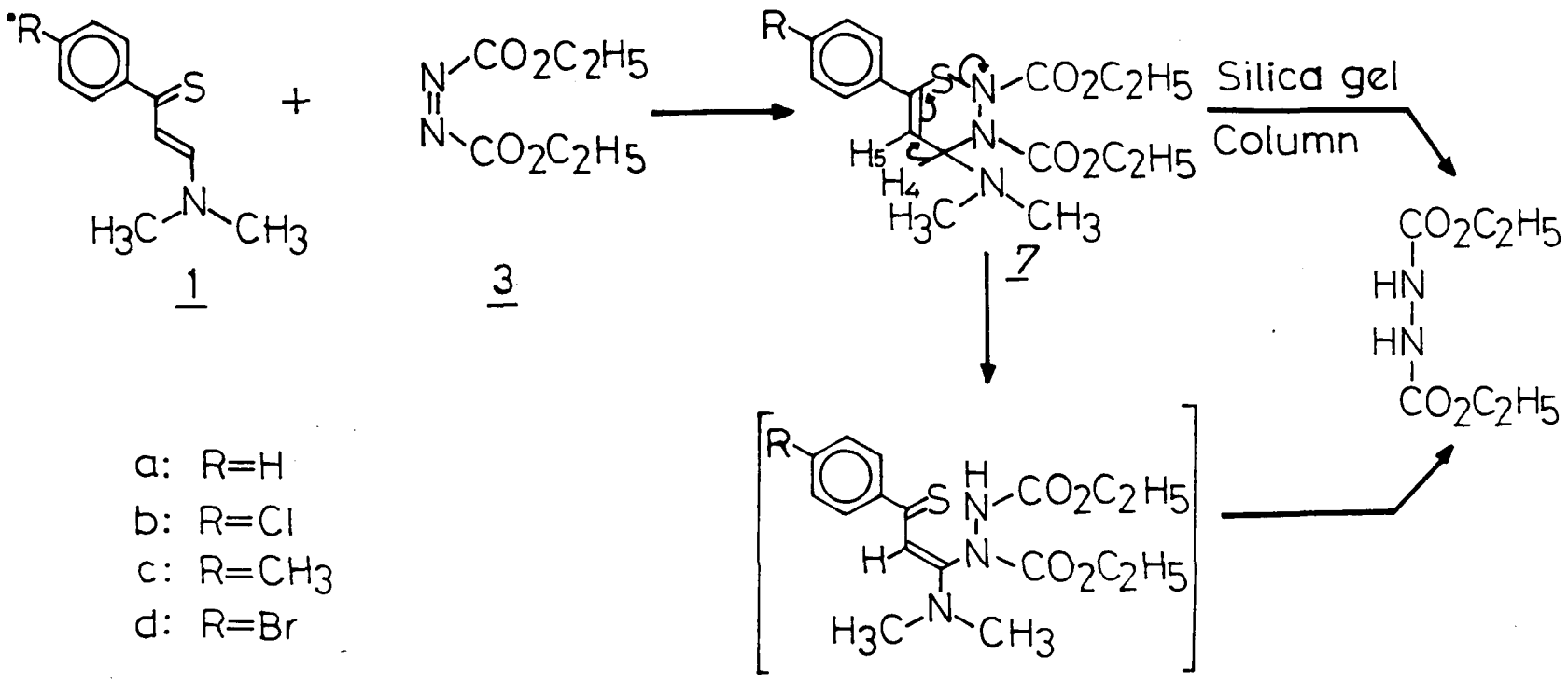
higher field probably due to the shielding effect of N-aryl function. The multiplet at δ 4.04 is assigned to methylene protons 'b', the multiplet at δ 4.36 is assigned to the other methylene protons and NH proton. This is supported by the appearance of a quartet due to the two methylene protons in this region in D_2O exchange ^1H NMR spectrum (Fig.2). The doublet at δ 6.00 is assigned to the vinylic proton H_d and the multiplet at δ 6.24 is assigned to the methine proton. This multiplet would be expected in view of the fact that H_c proton will be split both by H_d and -NH- proton. The D_2O exchange proton NMR further confirms this assignment which showed a quartet for H_c and H_d (J_{cd}=6 cps). Coupling constant value of J_{cd} of 6Hz indicate an equatorial position for H_c[21]. The doublet at δ 6.74 is assigned to the ortho protons of the aniline nucleus as one would expect these protons to appear at a higher field due to the electron donating ability of the amino function. Finally the group of partially resolved signals at δ 7.30 is assigned to the other aromatic protons. The PMR spectra of other thiadiazine derivatives are reported in table 1. Surprisingly the methylene protons marked 'b' appear as a multiplet, except in case of 4f where these appear as a quartet, in the PMR spectra of 4. The cause of this multiplicity is not well understood and could probably be due to the somehow non-equivalence of these

methylene protons.

Further support for the structure of 4a was obtained from the ^{13}C NMR spectrum assignments made with the help of coupled spectrum (Figs. 3 & 4). The methyl carbon attached to protons marked 'a' is assigned at δ13.55 whereas the other methyl carbon is observed at δ14.47. The methylene carbon attached to protons 'b' and the other methylene carbon are observed at δ 63.11 and 63.80 respectively. The carbons C-4, C-5 and C-6 are assigned at δ 61.51, 113.88 and 139.29 respectively. The signals at δ113.07 (one $^{3}J_{C,H}$ 7Hz in the coupled spectrum), 119.03 (two $^{3}J_{C,H}$ ~7Hz indicated by the splitting of each line of the doublet into a triplet), 134.47 (two $^{3}J_{C,H}$ ~7Hz), 139.29 and 144.31 (two $^{3}J_{C,H}$ ~7Hz) are assigned to  ,  ,  and  respectively. All other aromatic carbons are assigned at δ127.03, 129.08 and 130.08. Finally the two carbonyls are assigned at δ 154.74 and 155.23. Further confirmation about the structure of 4a was obtained from its mass spectrum which showed the absence of molecular ion peak and showed the peaks due to $M^{+}-S$, $M^{+}-C_6H_5-C{\equiv}C$, $M^{+}-2CO_2C_2H_5$ and  .

In continuation of our investigations we have examined the reactions of 3-N,N-dimethylamino-1-arylpropene-1-thiones (1) with ethyl azodicarboxylate (3). Thus the benzene solution of equimolar amount of 3 was added dropwise

to the benzene solution of 1 at room temperature. The reaction was complete within 10 minutes as indicated by the disappearance of the red colour of the thioamide vinylogs (1). The complete removal of the solvent under reduced pressure resulted in a viscous mass, the TLC of which showed traces of impurities. It defied all attempts of final purification and passing it through a silica gel column resulted in the isolation of ethyl hydrazodicarboxylate. The probable mechanism for the formation of ethyl hydrazodicarboxylate is outlined in Scheme 5. The viscous mass has been characterised as previously unknown 2,3-diethoxycarbonyl-4-N,N-dimethylamino-6-aryl-4H-1,2,3-thiadiazines (7) on the basis of spectral evidences. The IR spectrum of 7b, for example, showed carbonyl absorption bands around 1735 cm^{-1} and 1725 cm^{-1}. Its ^1H NMR spectrum showed superimposed triplets at δ 1.38(6H) due to two methyl protons, a singlet at δ 2.42(6H) due to $-N(CH_3)_2$ protons, two superimposed quartets at δ 4.35(4H) due to four methylene protons, a doublet at δ 5.57 due to methine proton H_4 ($J_{4,5}$ = 3Hz), another doublet at δ 5.94 due to vinylic proton H_5 ($J_{4,5}$=3Hz) and a group of unresolved signals at δ 7.40(4H) due to aromatic protons. The coupling constant value $J_{4,5}$ of 3Hz indicates an axial position for H_4. Further confirmation about the structure of 7b is obtained from its mass spectrum which showed the molecular ion peak at 399(7) and the other important peaks are observed at 366(3)(m^+-SH),



a: R=H
b: R=Cl
c: $R=CH_3$
d: R=Br

Scheme 5

326(3)($M^+-CO_2C_2H_5$), 299(16)(M^+-N_2-2CO), 264(21)(M^+-S, $-CO_2C_2H_5$, $-C_2H_5$), 225(36)(1b), 210(25)(1b-CH_3), 192(78) (1b-SH), 181(15)(1b-$N(CH_3)_2$), 157(44)(1b-$N(CH_3)_2$, -S) and 29(100)(C_2H_5).

The equatorial and axial orientation for H_4 in case of 4 and 7 respectively indicate the concerted nature of enamino-thiones cycloadditions with ethyl azodicarboxylate. The difference in coupling constants $J_{4,5}$ in case of 4 and 7 cannot be attributed to the difference in the substituted amino function at position-3 since in that case the $J_{4,5}$ for thiadiazine 7 should have been higher than that of thiadiazine 4[22].

2.3 EXPERIMENTAL SECTION:

All the melting points were determined on a "Toshniwal" melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer model 297 IR spectrometer. ^{1}H NMR traces were recorded on a Varian EM 390 90 MHz spectrometer.

Starting materials:

The commercial samples of 4-Chloroacetophenone, 4-bromoacetophenone, 4-methylacetophenone, aniline, o-chloroaniline, m-chloroaniline, p-chloroaniline, p-bromoaniline, o-toluidine and p-toluidine were purified before use.

N,N-Dimethylformamide dimethylacetal[23] and N,N-dimethylformamide diethylacetal[23] were prepared according to the known procedure.

General procedure for the preparation of 3-dimethylamino-1-arylpropene-1-one[19]:

A solution of 25g (0.19 mol) of 4-methylacetophenone in 50 ml of N,N-dimethylformamide diethylacetal (N,N-dimethylformamide dimethylacetal was used for 3-dimethylamino-1-phenylpropene-1-one, 3-dimethylamino-1-(4-chlorophenyl) propene-1-one and 3-dimethylamino-1-(4-bromophenyl) propene-1-one) was refluxed for 20 hours during which time some ethanol was formed and removed through condenser. After cooling the solution deposited yellow crystals of

3-dimethylamino-1-(4-methylphenyl)propene-1-one,m.p. 95°C (lit.[19] m.p. 95-96°C).

3-Dimethylamino-1-phenylpropene-1-one, m.p. 96-98°C, 3-dimethylamino-1-(4-chlorophenyl)propene-1-one,m.p. 84-86°C and 3-dimethylamino-1-(4-bromophenyl)propene-1-one, m.p. 75-77°C were prepared similarly.

General procedure for the preparation of 3-dimethylamino-1-arylpropene-1-thione[19]:

To a solution of 22.6g (0.12 mol) of 3-dimethylamino-1-(4-methylphenyl)propene-1-one in 80 ml of anhydrous dichloromethane at 0°C was added a solution of 11.2 ml(0.12 mol) of phosphorous oxychloride in 30 ml of anhydrous dichloromethane over a period of 2 minutes. The reaction mixture was then stirred at room temperature for 10 minutes during which period (γ-chloro-p-methylcinnamylidine) dimethylammonium phosphorodichloridate precipitated out from the reaction mixture as yellow crystals (if necessary the reaction mixture was scratched with a spatula to induce the precipitation of the phosphorodichloridate salt). The stirring was continued at room temperature for another 10 minutes and then at 0°C for 10 minutes. The yellow crystals were collected by filtration, washed with small amount of dry dichloromethane and added to a stirred ice cooled solution of 50.4g (0.3 mol) of sodium perchlorate in 100 ml of water. The reaction mixture was vigorously stirred at 0°C for 20 minutes.

The perchlorate separated out as yellow crystals was collected by filtration, washed with an ice-cold solution of 10g of sodium perchlorate monohydrate in 100 ml of water, dried by suction and then washed with 50 ml of cold ethanol followed by 50 ml of cold ether, m.p. 201-203°C.

The yellow perchlorate (56.3g) was added over a period of 3 minutes to a stirred ice cold mixture of N,N-dimethylformamide (250 ml) and a solution of sodium sulfide nonahydrate (35.0g, 0.146 mol) in 40 ml of water. The reaction mixture was stirred at room temperature for two hours and then diluted with 600 ml of water. After being cooled in a refrigerator over night, the solution deposited the reddish orange crystals of 3-dimethylamino-1-(4-methylphenyl)propene-1-thione (1), m.p. 135-136°C.

3-Dimethylamino-1-(4-chlorophenyl)propene-1-thione, m.p. 119-120°C; 3-dimethylamino-1-(4-bromophenyl)propene-1-thione, m.p. 118-119°C and 3-dimethylamino-1-phenylpropene-1-thione, m.p. 115-116°C were prepared similarly.

General procedure for the preparation of 3-anilino-1-phenylpropene-1-thione (2)[20a]:

A solution of 0.5g of 3-dimethylamino-1-phenylpropene-1-thione (1) and 0.36g of aniline in benzene (80 ml) was refluxed for 4 hours. The solvent was then removed under reduced pressure and the residue containing 3-anilino-1-phenylpropene-1-thione was recrystalised from ethanol,

m.p. 102 (lit.[20b] m.p. 105-6°C).

Similar procedure was followed for the preparation of 3-o-chloroanilino-1-phenylpropene-1-thione, m.p. 90°C: 3-m-chloroanilino-1-phenylpropene-1-thione, m.p. 118°C: 3-p-chloroanilino-1-phenylpropene-1-thione, m.p.129°C: 3-p-bromoanilino-1-phenylpropene-1-thione, m.p. 138°C: 3-o-toluidino-1-phenylpropene-1-thione, m.p. 82°C (lit.[20a] m.p. 84-85°C); 3-p-toluidino-1-phenylpropene-1-thione, m.p. 140°C (lit.[20a] m.p. 142-145°C).

Procedure for the preparation of Ethyl azodicarboxylate:

A. Ethyl hydrazodicarboxylate[24]:

In a 3-1 three necked flask, equipped with a mechanical stirrer, two 500 ml dropping funnels and a thermometer, is placed a solution of 75g (1.5 mol) of 100% hydrazine hydrate in 750 ml of 95% ethanol. The reaction flask is cooled in an ice bath and 326g(3 mol) of ethyl chloroformate is added dropwise with stirring a rate sufficient to maintain the temperature between 15° to 20°. After exactly one half of the ethyl chloroformate has been introduced, a solution of 159g (1.5 mol) of sodium carbonate in 750 ml of water is added dropwise simultaneously with the remaining ethyl chloroformate. The addition of these two reactants is regulated so that the temperature does not rise above 20°. The addition of the chloroformate is completed slightly

in advance of the sodium carbonate, thus maintaining an excess of the chloroformate in the solution at all times. During the course of addition of the reagents, a precipitate is formed.

After addition of the reactants is complete, the walls of the flask are washed down with 200 ml of ice cold water and the reaction mixture is allowed to stirr for 30 minutes. The precipitate is then collected on a Buchner funnel, washed well with about 1 lit. of cold water and dried in a vacuum desiccator. The product melts at 131-133°C.

B. Ethyl azodicarboxylate:

A mixture of 20g of ethyl hydrazodicarboxylate in 12.5 ml of 70% nitric acid is placed in a 1 lit. three necked flask equipped with mechanical stirrer, gas out let tube and thermometer. The flask is cooled in an ice bath and when the temperature of the solution reaches 5°, cold yellow fuming nitric acid (90-95% HNO_3) (22 ml) is added. The reaction temperature is maintained at 0-5° for two hours with stirring and the reaction mixture is then carefully poured on a stirred mixture of 50g of ice, 50 ml of ice water and 10 ml of methylene chloride. After melting of ice the solution is transferred carefully to a 2 lit. separatory funnel. The organic (lower) layer is removed and the acid layer is

extracted with three 10 ml portions of methylene chloride. The combined organic layers are washed with 10 ml portions of ice water and are then stirred mechanically for 10 minutes with 50 ml of ice cold 10% potassium bicarbonate solution. The organic layer is finally washed with 10 ml of ice water and dried quickly with a small portions of anhydrous magnesium sulfate. The solution is then dried over night with a fresh portion of anhydrous magnesium sulfate. The methylene chloride is then removed on a steam bath under reduced pressure and the residue is rapidly distilled under vacuum (1-5 mm) from a flask immersed in an oil bath whose temperature is raised gradually from 75° to 130°. The crude distillate is then fractionally distilled under vacuum using an oil bath to heat the distillation flask. The main fraction is collected at $93-95^{\circ}/5$ mm.

General procedure for the reactions of 3-anilino-1-phenylpropene-1-thione with ethyl azodicarboxylate:

To a stirred solution of 3-anilino-1-phenylpropene-1-thione (0.48g, 0.002 mol) in dry benzene (15 ml) was added a benzene solution (5 ml) of ethyl azodicarboxylate (0.35g, 0.002 mol) and the reaction mixture was stirred at room temperature for 10 minutes. The oily residue obtained after the removal of the solvent under reduced pressure was stirred with hexane. The solid so obtained 0.6g (70%) was filtered and

recrystallised from a mixture (1:1) of benzene and hexane and was characterised as 2,3-diethoxycarbonyl-4-anilino-6-phenyl-4H-1,2,3-thiadiazine, m.p. 118°C: IR(KBr) ν_{max}: >C=O 1730 cm^{-1}, 1715 cm^{-1}; C=C 1605 cm^{-1}; NH 3375 cm^{-1}; Analysis calculated for $C_{21}H_{23}N_3O_4S$: C,61.02; H,5.56; N,10.17%; Found: C,60.75; H,5.35: N,10.20%. ^1H NMR($CDCl_3$) δ_{ppm}: 0.83(t,3H,-O-$\overset{1}{C}_i$-CH_{3a}); 1.33(t,3H,CH_3); 4.04(m,$2H_b$); 4.36(m,3H,-OCH_2- and NH); 6.00(d,1H,H_d,J=6Hz), 6.24(m,1H, H_c); 6,74(d,2H,-N(H)- ); 7.30(m,8H,aromatic).

The reactions of other substituted 3-N-arylamino-1-phenyl-propene-1-thione with ethyl azodicarboxylate were carried out by following the same procedure (Table 1 and 2).

General Procedure for the reactions of 3-N,N-dimethylamino-1-arylpropene-1-thiones with ethyl azodicarboxylate:

To a stirred solution of 3-N,N-dimethylamino-1-arylpropene-1-thione (0.002 mol) in dry benyene (15 ml) was added a benzene solution (5 ml) of ethyl azodicarboxylate (0.002 mol) and the reaction mixture was stirred at room temperature for 10 minutes. The complete removal of the solvent under reduced pressure yielded quantitative amount of a viscous mass which was washed with cold petroleum ether (40-60°), dried under reduced pressure and characterised as 2,3-diethoxycarbonyl-4-dimethylamino-6-aryl-4H-1,2,3-thiadiazines (Table 3).

Table 1: Physical and analytical data for compounds 4a-4g

Compound	R	m.p. °C	Yield %	Calc. Found	Analysis % C	H	N	S
4a	H	118	70		61.02	5.56	10.17	7.75
					60.75	5.35	- 10.20	7.72
4b	o-Cl	78	75		56.37	4.92	9.40	
					56.50	4.86	9.15	
4c	m-Cl	144-146	75		56.37	4.92	9.40	
					56.45	4.93	9.32	
4d	p-Cl	138	88		56.37	4.92	9.40	
					56.43	4.81	9.27	
4e	p-Br	140	92		51.22	4.47	8.54	
					51.52	4.56	8.82	
4f	o-CH_3	98-100	76		61.83	5.85	9.84	7.49
					61.97	5.97	9.81	7.45
4g	p-CH_3	120-122	90		61.83	5.85	9.84	7.49
					61.86	5.96	9.63	7.36

Table 2: Spectral data for compounds 4a-4g

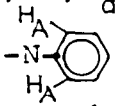
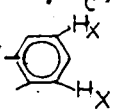
Compound	R	IR(KBr) ν_{max} cm^{-1}	^1H NMR ($CDCl_3$) δppm
4a	H	3375, 1730, 1715, 1605	0.83(t,3H,$-O-\overset{H_a}{\overset{|}{C}}-CH_3$), 1.33(t,3H,$CH_3$), 4.04 (m,2$H_b$), 4.36(m,3H,$-CH_2-$ and NH), 6.00 (d,1H,H_d,J=6Hz), 6.24(m,1H,H_c), 6.74(d, 2H,  ,J=8Hz), 7.30(m,8H,Ar-H)
4b	o-Cl	3375, 1735, 1715, 1600	0.82(t,3H,$-O-\overset{H_a}{\overset{|}{C}}-CH_3$), 1.32(t,3H,$CH_3$), 3.90 (m,2$H_b$), 4.33(m,3H,$-CH_2-$ and NH), 6.03 (d,1H,H_d, J=6Hz), 6.26(m,1H,H_c), 7.02(m, 9H,Ar-H)
4c	m-Cl	3375, 1730, 1715, 1600	0.93(t,3H,$-O-\overset{H_a}{\overset{|}{C}}-CH_3$), 1.43(t,3H,$CH_3$), 4.00 (m,2$H_b$), 4.45(q,2H,$-CH_2-$), 4.56(b,1H,NH), 6.10(d,1H,H_d,J=6Hz), 6.24(m,1H,H_c), 7.17 (m,9H,Ar-H)
4d	p-Cl	3380, 1740, 1720, 1600	0.86(t,3H,$-O-\overset{H_a}{\overset{|}{C}}-CH_3$), 1.33(t,3H,$CH_3$), 3.90 (m,2$H_b$), 4.33(q,2H,$-CH_2-$), 4.56(b,1H,NH), 6.00(d,1H,H_d,J=6Hz), 6.23(m,1H,H_c), 6.76 (d,2H, ), 7.12(d,2H,  , J_{AX}= 8Hz), 7.30(m,5H,C_6H_5)

Table 2: Contd..2/-

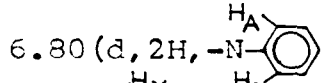
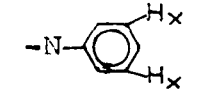
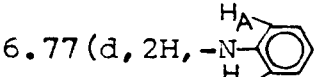
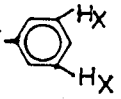
Compound	R	IR(KBr) ν_{max} cm^{-1}	^1H NMR($CDCl_3$) δppm
4e	p-Br	3385, 1740, 1720, 1600	0.92(t,3H,-O-C(a)-CH_3), 1.40(t,3H,CH_3), 4.10(m,2H_b), 4.44(q,2H,-CH_2), 4.58(b,1H, NH), 6.06(d,1H,H_d,J=6Hz), 6.26(m,1H,H_c), 6.80(d,2H,  ,J=8Hz), 7.40(m,7H,  and C_6H_5)
4f	o-CH_3	3375, 1730, 1715, 1600	0.83(t,3H,-O-C(a)-CH_3), 1.33(t,3H,CH_3), 2.13 (s,3H,CH_3-Ar), 3.87(q,2H_b), 4.26(m,3H, -CH_2- and NH), 6.06(d,1H,H_d,J=6Hz), 6.33 (m,1H,H_c), 7.16(m,9H,Ar-H)
4g	p-CH_3	3375, 1730, 1720, 1600	0.83(t,3H,-O-C(a)-CH_3), 1.32(t,3H,CH_3), 2.25 (s,3H,H_3C-Ar), 3.97(m,2H_b), 4.32(q,2H,- CH_2-), 4.17(b,1H,NH), 6.10(d,1H,H_d,J=6Hz), 6.28(dd,1H,H_c), 6.77(d,2H, ), 7.04 (d,2H,  ,J_{AX}=8Hz), 7.46(m,5H,C_6H_5)

Table 3: Spectral data for compounds 7e-7d

Compound	R	IR(KBr) ν_{max} cm^{-1}	Molecular formula (M^+)	^1H NMR($CDCl_3$) δ ppm
7a	H	1735, 1725	$C_{17}H_{23}N_3O_4S$ (365)	1.30(m,6H,$2CH_3$), 2.33(s,6H,-$N(CH_3)_2$), 4.20(m,4H,$2CH_2$), 5.50 (d,1H,H_4,J=3Hz), 5.90(d,1H,H_5, $J_{4,5}$=3Hz), 7.13(m,5H,Ar-H)
7b	Cl	1735, 1725	$C_{17}H_{22}ClN_3O_4S$ (399)	1.38(m,6H,$2CH_3$), 2.42(s,6H, $N(CH_3)_2$), 4.35(m,4H,$2CH_2$), 5.57 (d,1H,H_4,$J_{4,5}$=3Hz), 5.94(d,1H, H_5,$J_{4,5}$=3Hz), 7.40(m,4H,Ar-H)
7c	CH_3	1735, 1725	$C_{18}H_{25}N_3O_4S$ (379)	1.30(m,6H,$2CH_3$), 2.30(s,6H, $N(CH_3)_2$), 2.40(s,3H,H_3C-Ar), 4.20(m,4H,$2CH_2$), 5.53(d,1H,H_4, J=3Hz), 5.90(d,1H,H_5,J=3Hz), 7.30(m,4H,Ar-H)
7d	Br	1740, 1730	$C_{17}H_{22}BrN_3O_4S$ (444)	1.33(m,6H,$2CH_3$),2.36(s,6H,-$N(CH_3)_2$), 4.23(m,4H,$2CH_2$), 5.43 (d,1H,H_4,J=3Hz), 5.90(d,1H,H_5, $J_{4,5}$=3Hz), 7.35(m,4H,Ar-H)

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CHAPTER III

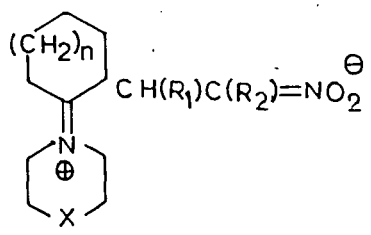
REACTIONS OF THIOAMIDE VINYLOGS (ENAMINO-THIONES) WITH NITROALKENES, NITROSOALKENES, DICYCLOPENTADIENE AND NORBORNYLENE

3.1 INTRODUCTION:

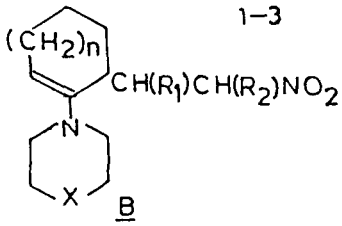
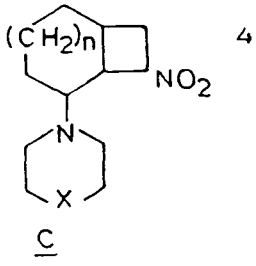
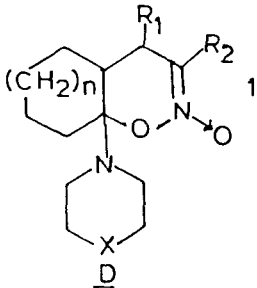
As discussed in chapter I the thioamide vinylogs have been known to participate as 4π component in a large variety of Diels-Alder cycloadditions with carbon-carbon dienophiles. Also, nitroalkenes have been reported to

participate as 2π or 4π components in a variety of cycloaddition reactions. The reactions of enamines with nitroolefins have been studied in detail and it has been observed that the products depend upon the choice of enamine, substituents in the nitroolefins and the conditions used[1-4]. The reactions of 1:1 cycloalkanone derived enamines and nitroolefins lead to three types of 1:1 adducts via the Zwitterion intermediate A (Table 1). With substituted nitroolefins lacking an α-substituent, C-protonation, which is usually observed in polar solvents such as acetonitrile, results in substituted acyclic nitroalkane (B). In non-polar solvents such as hexane intramolecular reactions are favoured only with nitroethylene and C-alkylation leads to bicyclic nitrocyclobutane (C).

Table 1: Reactions of 1:1 cycloalkanoneenamine-nitroolefin Zwitterion intermediate adduct in aprotic solvents.



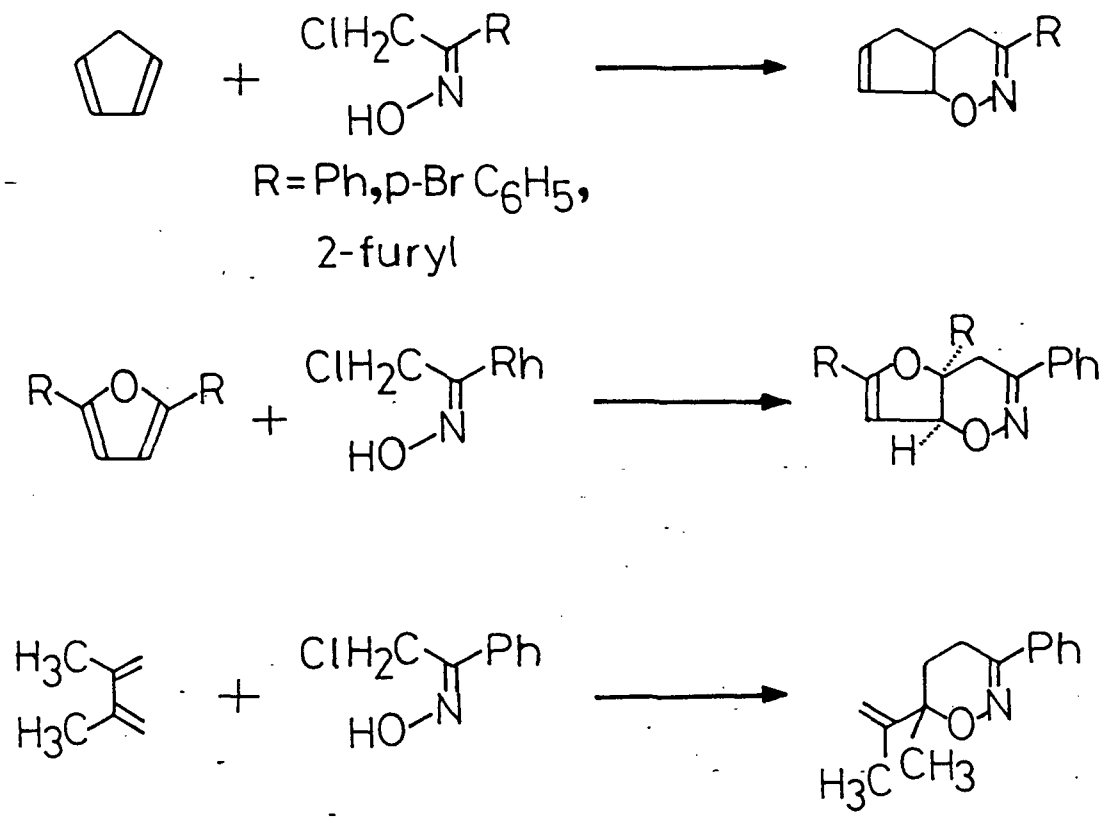
A (X=O, —)

R_1	R_2	n	Aprotic solvent type	Reaction type	Product	Ref.
Aryl, Alkyl,H	H	n	Polar	C-protonation	 B	1-3
Aryl, Alkyl,H	Aryl alkyl	>2	Polar or non-polar	C-protonation	B	
H	H	0,1	Non-polar	Intramolecular C-alkylation	 C	4
Aryl, Alkyl,H	Aryl Alkyl	0,1,2	Polar or Non-polar	Intramolecular O-alkylation	 D	1

The α-substituted nitroolefins with enamines from cycloalkanones of less than eight membered ring, in polar or non-polar aprotic solvents lead to cyclic nitronic esters (D) via intramolecular O-alkylation of Zwitterion A. Interestingly, acyclic enamines do not give cyclic nitronic esters and instead produce substituted nitroalkanes and nitrocyclobutanes with nitroolefins[5]. The (4+2) cycloaddition reactions of nitroolefins and cyclopentadiene have also been reported in which nitroolefins participate as 2π component[6].

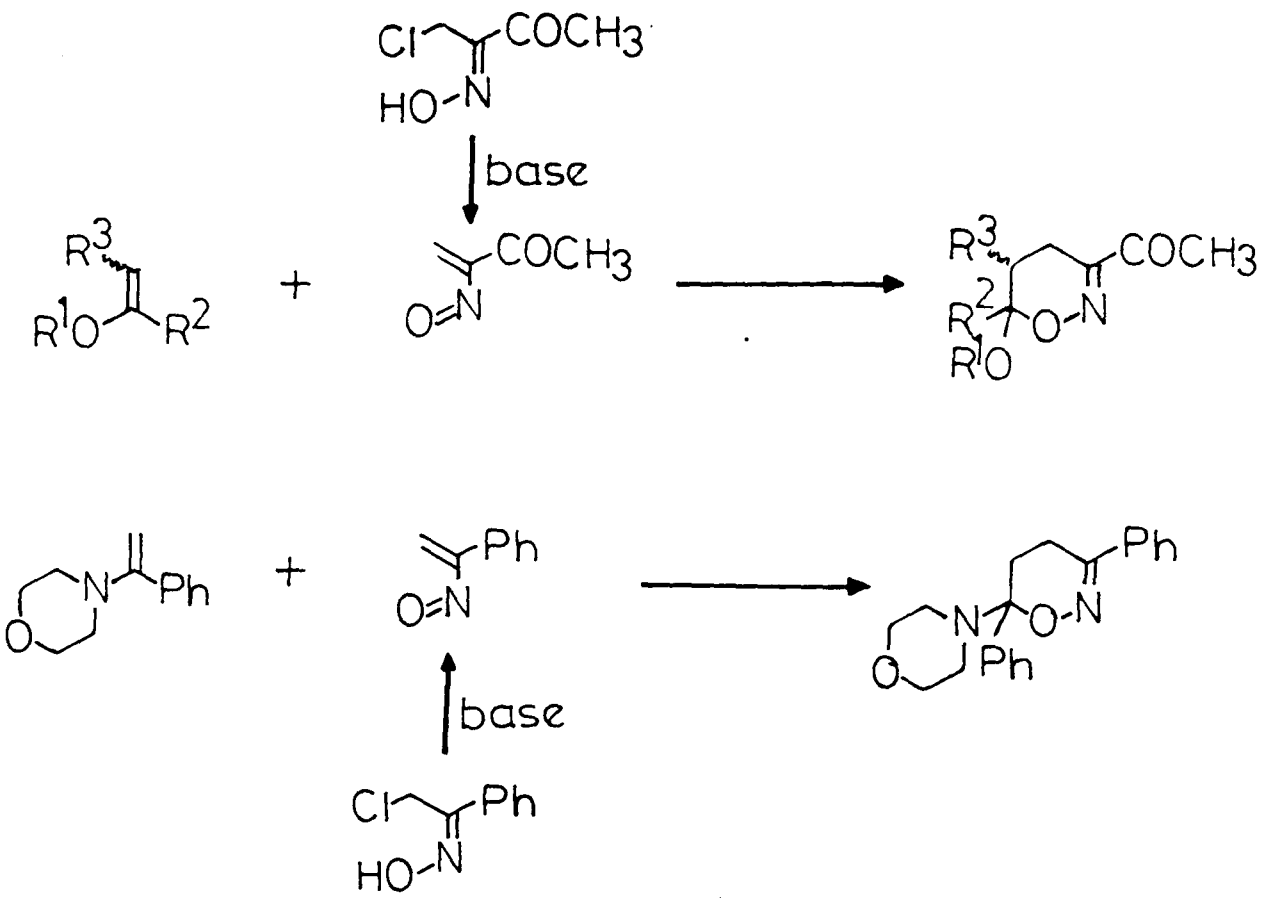
Nitrosoalkenes are usually isolable only if substituted with bulky alkyl[7] or aryl[8] groups, but have been trapped as intermediate in a variety of cycloaddition reactions wherein these behave as a 4π or 2π components. Gilchrist et al on the basis of the comparison of orbital energies and orbital co-efficients of nitrosoethylene and butadiene have clearly indicated that the major interaction is likely to be that between the HOMO of diene and LUMO of nitrosoethylene i.e. butadiene acts as the donor and nitrosoethylene as acceptor[9].

Gilchrist and Faragher[9] have investigated the cycloaddition reactions of nitrosoethylene and other simple nitrosoalkenes with dienes such as cyclopentadiene, furan and 2,3-dimethylbutadiene. In all these reactions, nitrosoalkenes behave as 4π component (Scheme 1). The adduct so formed



Scheme 1

was isolable with α-nitroso styrene, whereas the one formed from the reaction of nitrosoethylene with cyclopentadiene was unstable. They also observed another mode of addition of nitrosoalkene i.e. via N=O bond in the reaction between 2,2-dichloronitrosoethylene and cyclopentadiene, but the adduct so formed was unstable. The adducts 1,2-oxazines, which possess the inherent weakness of the N-O bond were further used as the precursors for other heterocyclic and acyclic systems[12,13]. The nitrosoalkenes have also been found to behave as 4π components in cycloaddition reactions with electron rich olefins such as enol ethers[10] and enamines[11] (Scheme 2). The reactions of nitroalkenes, nitrosoalkenes with enamines, cyclopentadiene and cyclohexadiene have been well investigated but there are no reports concerning the reactions of nitrosoalkenes and nitroalkenes with heterodienes. We have investigated the reactions of nitroalkenes and nitrosoalkenes with enamino-thiones in order to examine the reaction pathway followed and the nature of the products formed in these cases. As the examples of cycloaddition reactions of heterodienes with alkenes unsubstituted by a polar electron donating (or withdrawing) are very rare. We have investigated the reactions of enamino-thiones with dicyclopentadiene and norbornylene. The results of all these investigations are presented here.

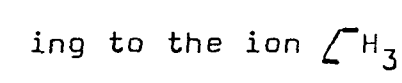

Cl
COCH3
HO-N
base
R3
R1O
R2
+
O=N
COCH3
R3
COCH3
R2
R1O
O-N
10
Ph
+
O=N
Ph
base
Cl
Ph
HO-N
Ph
N
O-N
O
Ph
11

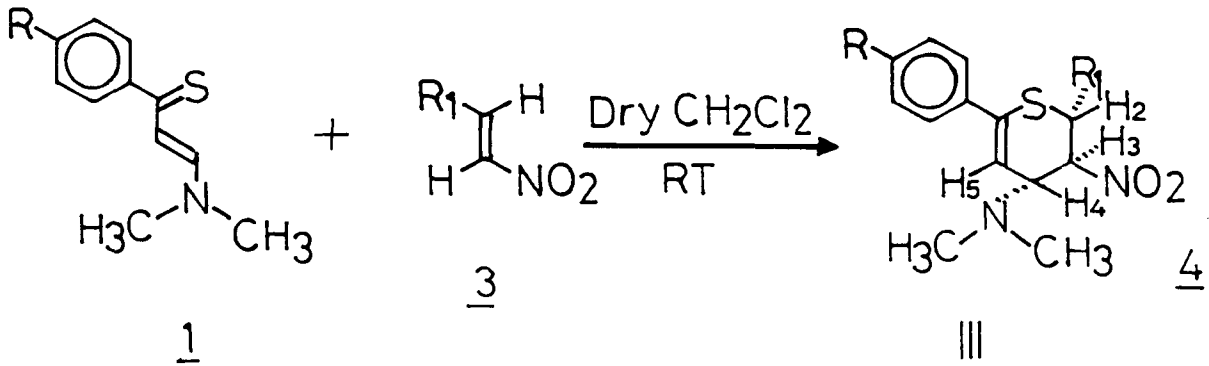
Ref.

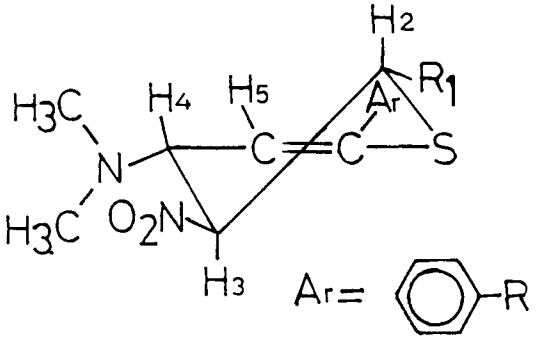
Scheme 2

3.2 RESULTS AND DISCUSSIONS:

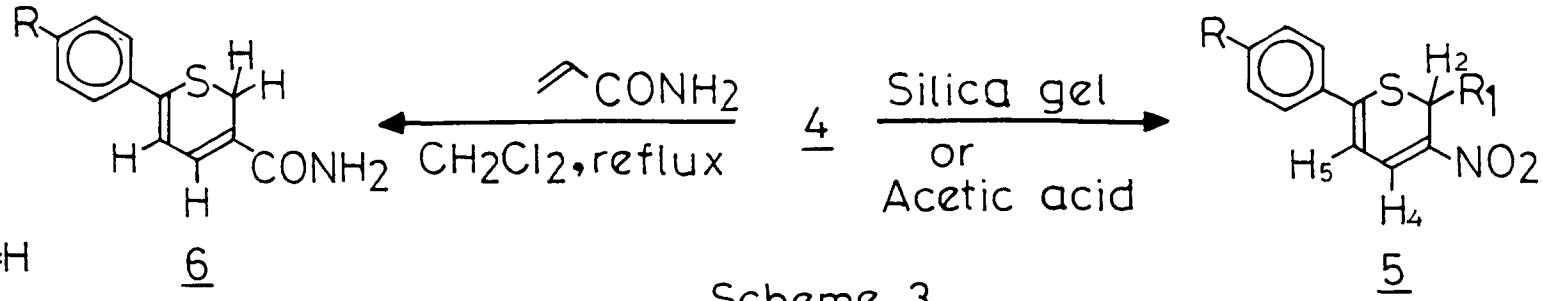
3.2.1 Reactions of thioamide vinylogs (enaminothiones) with nitroalkenes :

The reactions of 3-dimethylamino-1-arylpropene-1-thione(1) with ß-nitroalkenes (3) in methylene chloride at room temperature resulted in the stereospecific formation of (2S,3R,4R)-6-aryl-2-aryl/furyl-3,4-dihydro-4-dimethylamino-3-nitro-2H-thiopyranes (4) in good yields (78-93%). The cycloadducts 4 are formed by (4+2) cycloaddition reaction of 1 and 3 in which thioamide vinylogs (1) participate as 4π components. The cycloadducts 4 are characterized on the basis of analytical and spectral evidences. The cycloadduct 4a, for example, analysed for $C_{20}H_{22}N_2O_2S$. Its mass spectrum showed the absence of molecular ion peak but exhibited strong peaks due to retero Diels-Alder fragments at m/z 205 corresponding to the ion  and at m/z 149 due to $[H_5C_6-CH=CH-NO_2]^+$. Further proof for its structure could be obtained from its ^1H NMR spectrum ($CDCl_3$) δppm which showed two singlets at δ 2.33(3H) and 2.66(6H). The singlet at δ 2.33 is assigned to three methyl protons of $H_3C-C_6H_4$ whereas the one at δ 2.66 is assigned to six protons of $-N(CH_3)_2$. The doublet of doublet at δ 4.26($J_{H_3H_4}$ = ~11 Hz; $J_{H_4H_5}$ = ~3Hz), the doublet at δ 4.79($J_{H_2H_3}$ = ~11Hz), another doublet of doublet at δ5.26($J_{H_2H_3}$ = ~11Hz, $J_{H_3H_4}$ = ~ 11Hz) and the





4a: R=CH3 , R1=C6H5
b: R=CH3 , R1=p-OCH3C6H4
c: R=CH3 , R1 = 
d: R=Cl , R1=C6H5
e: R=Cl , R1=p-OCH3C6H4
f: R=Cl , R1 = 
g: R=H , R1=C6H5
h: R=H , R1=p-OCH3C6H4
i: R=H , R1 = 

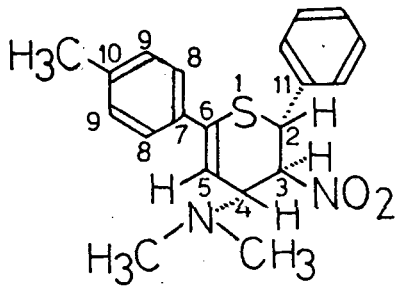


Scheme 3

doublet at δ 6.00 (JH_4H_5 = ~3Hz) are assigned to the protons H_4, H_2, H_3 and H_5 respectively. The nine aromatic protons are observed as a multiplet at δ 7.06-7.13. The coupling constants JH_2H_3 = ~11Hz and JH_3H_4 = ~11Hz indicate a trans diaxial configuration for H_2H_3 and H_3H_4. Also, the coupling constant value JH_4H_5 of about 3Hz indicate an axial orientation for H_4[14].

To our knowledge this is the first known case of cycloaddition reactions of thioamide vinylogs where the stereochemistry at C-2, C-3 and C-4 could be clearly defined, since in most of the cycloaddition reactions of thioamide vinylogs the initial cycloadducts very rapidly undergo elimination of dimethylamine. The values of the coupling constant between H_2H_3, H_3H_4 and H_4H_5 are consistent with a stereochemistry which results from a concerted cycloaddition of the thioamide vinylogs E-isomer with β-nitrostyrene. Its infrared spectrum (KBr) showed strong absorptions at 1610 and 1550 cm^{-1} due to C=C and NO_2 stretchings. The final proof for the structure of 4a was obtained from its ^{13}C NMR spectral assignments made with the help of off resonance decoupled spectrum. Its decoupled ^{13}C NMR spectrum exhibited the peaks at δ21.07 ($Ar-CH_3$), 40.51 ($-N(CH_3)_2$), 49.02 (C-2), 65.99(C-4), 89.29(C-3), 115.54(C-5), 139.02(C-6 or C-7), 138.20(C-7 or C-6), 134.85(C-10 or C-11) and

134.15(C-10 or C-11). The other aromatic carbons are



4a

observed at δ 126.34, 127.34, 128.34, 128.98 and 129.28.

Interestingly the white crystalline cycloadducts 4 result in dark red solution when dissolved in chloroform or methylene chloride at room temperature and the unchanged white cycloadducts are recovered on evaporation of the dark red solution. This is probably due to retro Diels-Alder dissociation of 4 to 1 and 3 in chloroform/methylene chloride solution which is supported by the following observations:

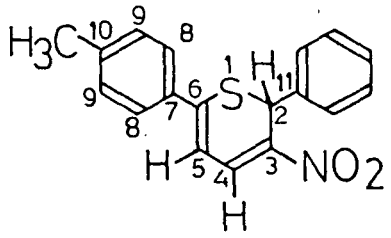
(i) Disappearance of the red colour when other dienophiles like dimethylacetylene dicarboxylate are added to the methylene chloride solution of 4.

(ii) Isolation of thiopyran derivative 6 by refluxing equimolar amounts of 4 and acrylamide in methylene chloride.

The product 6 is identified by its undepressed melting point and superimposable IR spectrum with that of authentic sample[15]. The dissociation of 4 to 1 and 3 appears to be slower in non-polar solvents like benzene since the solution of 4 in benzene slowly starts turning yellowish and becomes red only on prolonged heating.

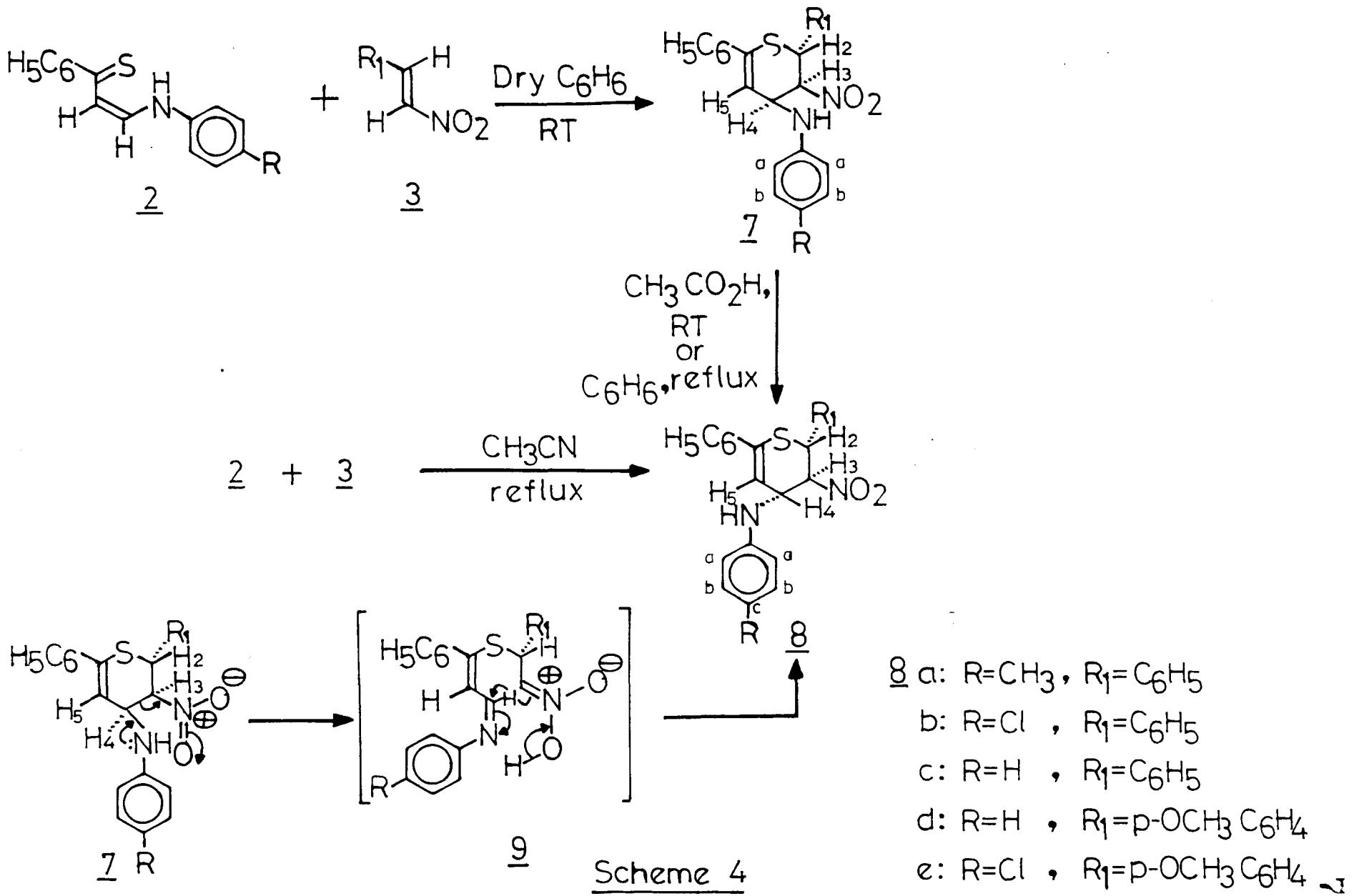
The cycloadducts 4 undergo elimination of dimethylamine, on eluting it through silica gel column and on stirring its methylene chloride solution with few drops of acetic acid resulting in good yields (65-80%) of hitherto unknown red crystalline 6-aryl-2-aryl(furyl)-3-nitro-2H-thiopyrans (5). It is worthwhile to mention here that in presence of bases like triethylamine the benzene/methylene chloride solutions of 4 undergo very slow elimination of dimethylamine even under refluxing conditions. This fact probably also indicates cis stereochemistry for H_3 and $-N(CH_3)_2$. The formation of the adducts 4, 5 and 6 in these reactions is outlined in Scheme 3. The products after the elimination of dimethylamine were characterized as thiopyran derivatives 5 on the basis of analytical and spectral evidences. For example, 5a analysed satisfactorily for $C_{18}H_{15}NO_2S$. Its ^1H NMR spectrum showed two singlets at δ 2.36 and 5.69. The singlet at δ2.36 is assigned to three methyl protons of $H_3C-C_6H_4$ and the one at δ5.69 is due to the

proton H_2. Two doublets at δ 6.63 (J=7-8Hz) and δ 8.00 (J=7-8Hz) are assigned H_5 and H_4 respectively. The nine aromatic protons are observed as a multiplet in the region δ 7.13-7.50. Its mass spectrum exhibited the molecular ion peak at m/z 309(M^+). Further structural proof for 5a was obtained from its decoupled ^{13}C NMR spectrum which showed the peaks at δ 21.31 (H_3C-Ar), 39.98(C-2), 113.31(C-5), 147.42 (C-3), 141.38(C-6 or C-7), 139.79 (C-6 or C-7), 136.76(C-10 or C-11) and 133.09(C-10 or C-11). Other aromatic carbons and C-4 are observed at δ 126.46, 127.57, 127.98, 128.39, 128.75, 129.51 and 131.15.



5a

In continuation of our studies, we have examined the reactions of nitroalkenes with 3-N-arylamino-1-phenyl-propene-1-thiones (2) in which the preferred geometry involves intramolecular hydrogen bonding between NH and sulphur of thione. The treatment of thioamide vinylogs (2) with ß-nitroalkenes (3) in anhydrous benzene


2
3
Dry C6H6
RT
7
CH3CO2H,
RT
or
C6H6, reflux
2 + 3
CH3CN
reflux
8
7 R
9
Scheme 4
8 a: R=CH3, R1=C6H5
b: R=Cl , R1=C6H5
c: R=H , R1=C6H5
d: R=H , R1=p-OCH3 C6H4
e: R=Cl , R1=p-OCH3 C6H4

gave (70-78%) of previously unknown (2S,3R,4S)-2-aryl-4-arylamino-3-nitro-6-phenyl-3,4-dihydro-2H-thiopyrans(7). The structure 7 has been assigned to products on the basis of analytical data and spectral evidences. Compound 7a, for example, analysed for $C_{24}H_{22}N_2O_2S$. Its mass spectrum showed the absence of molecular ion peak and exhibited strong peaks at m/z 149 and m/z 253 corresponding to the ions $\angle^{-}C_6H_5-CH=CH-NO_2\_7^{+}$ and $\angle^{-}C_6H_5-\overset{S}{\underset{H}{C}}-CH=CH-\underset{H}{N}-$  $\_CH_3\_7^{+}$ respectively. Its IR spectrum (KBr) showed absorption peaks at 3400 cm^{-1}(ν_{NH}), 1610 cm^{-1} ($\nu_{C=C}$) and 1545 cm^{-1}(ν_{NO_2}). The ^1H NMR spectrum ($CDCl_3$) δppm of compound 7a showed one singlet at δ 2.20 which corresponds to three methyl protons and one broad doublet at δ 3.76, exchangeable with D_2O, is assigned to NH proton. A multiplet, changing to a clear dd on D_2O exchange, at δ 4.80 (JH_3H_4=4Hz, JH_4H_5=6Hz) could be assigned to H_4. The doublet at δ 5.00(JH_2H_3=10-11Hz) is assigned to H_2. The doublet of doublet at δ 5.36(JH_2H_3=10-11Hz; JH_3H_4= 4Hz) is assigned to the proton H_3. The doublet at δ 6.18 (JH_4H_5=6Hz) is due to the vinylic proton H_5. The two doublets at δ 6.50 and 6.96 with a coupling constant of 8Hz are assigned to the protons H_a and H_b respectively. Other ten aromatic protons are observed in the region δ 7.13-7.60. The values of coupling constants between H_2H_3, H_3H_4 and H_4H_5 are consistant with a stereochemistry

which results from a cycloaddition of z-isomer of thioamide vinylogs (2) involving an endo transition state. We can therefore conclude that the addition of 2 and 3 is concerted and results in stereospecific product 7. The coupling constant values JH_2H_3 and JH_3H_4 of 10-11Hz and 4Hz respectively indicate trans diaxial arrangement for H_2H_3 and axial-equatorial arrangements for H_3 and H_4 respectively. Further more the coupling constant value JH_4H_5 of 6Hz also indicate an equatorial orientation for H_4.

The kinetically controlled products 7 having equatorial NO_2 at C-3 and axial -NH-Ar at C-4, change to more stable products 8 having equatorial-NO_2 and -NH-Ar at C-3 and C-4 under the following reaction condition:

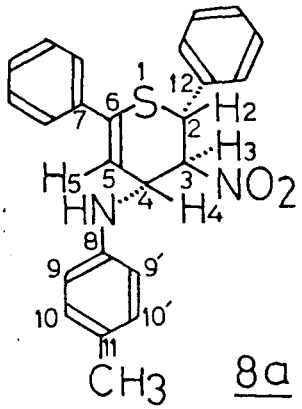
(i) Stirring a solution of 7 in dry benzene containing few drops of acetic acid at room temperature for five hours.

(ii) By refluxing a solution of 7 in dry benzene for ten hours.

It is worthwhile to mention here that the same products 8 have been obtained directly by refluxing a solution of 2 and 3 in dry benzene/acetonitrile. The reaction is much more faster in acetonitrile as it takes about five hours in acetonitrile whereas it takes about ten hours in benzene.

The structure 8 has been assigned on the basis of analytical and spectral data. The analytical results indicated that compound 8a has molecular formula $C_{24}H_{22}N_2O_2S$. Its mass spectrum exhibited the molecular ion peak at m/z 402 and peaks due to retro Diels-Alder fragments at m/z 253 and m/z 149. Its IR spectrum showed absorption bands at 3400 cm^{-1} (broad -NH), 1610 cm^{-1} ($\nu_{C=C}$) and 1550 cm^{-1} (ν_{NO_2}). The characteristic evidence in support of assigned structure 8a was obtained from its ^1H NMR spectrum. The singlet at δ 2.23 and a broad doublet at δ 3.63, exchangeable with D_2O, are assigned to the three methyl protons and -NH proton respectively. The doublet at δ 4.95($J_{H_2H_3}$ = ~11Hz) is assigned to the proton H_2. A multiplet converting to a dd on D_2O exchange, at δ 5.09 could be assigned to proton H_4 ($J_{H_4H_5}$ = ~3Hz; $J_{H_3H_4}$ = ~11Hz). Another doublet of doublet at δ 5.31 have been assigned to proton H_3 ($J_{H_2H_3}$ = $J_{H_3H_4}$ = ~11Hz). The vinylic proton H_5 appeared as a doublet at δ 6.03 ($J_{H_4H_5}$ = 3Hz). The two doublets at δ 6.63 and δ 7.02 are assigned to two protons H_1 and two protons H_b ($J_{H_aH_b}$ = 8Hz) respectively. The multiplet in the region δ 7.13-7.53 is due to the ten aromatic protons. The coupling constant values $J_{H_2H_3}$ and $J_{H_3H_4}$ of about 11Hz indicate trans diaxial arrangements for H_2, H_3 and H_3, H_4. Also, the coupling constant value $J_{H_4H_5}$ of 3Hz indicate an axial orientation for H_4.

Further proof for the structure of 8a was obtained from its ^{13}C NMR ($CDCl_3$) δppm spectral assignments made with the help of off resonance decoupled spectrum. It showed peaks at δ 20.37(H_2C-Ar), 49.02(C-2), 57.01 (C-4), 91.23(C-23), 115.12(C-9 and C-9′), 119.47(C-5), 129.98(C-11), 133.80(C-12), 136.73(C-6 or C-7), 137.15 (C-6 or C-7) and 142.90(C-8). Other aromatic carbons are observed at δ126.46, 128.48, 128.63, 129.16 and 129.34. The formation of thiopyran derivatives 7 and 8 in these cases is outlined in Scheme 4. The conversion



8a

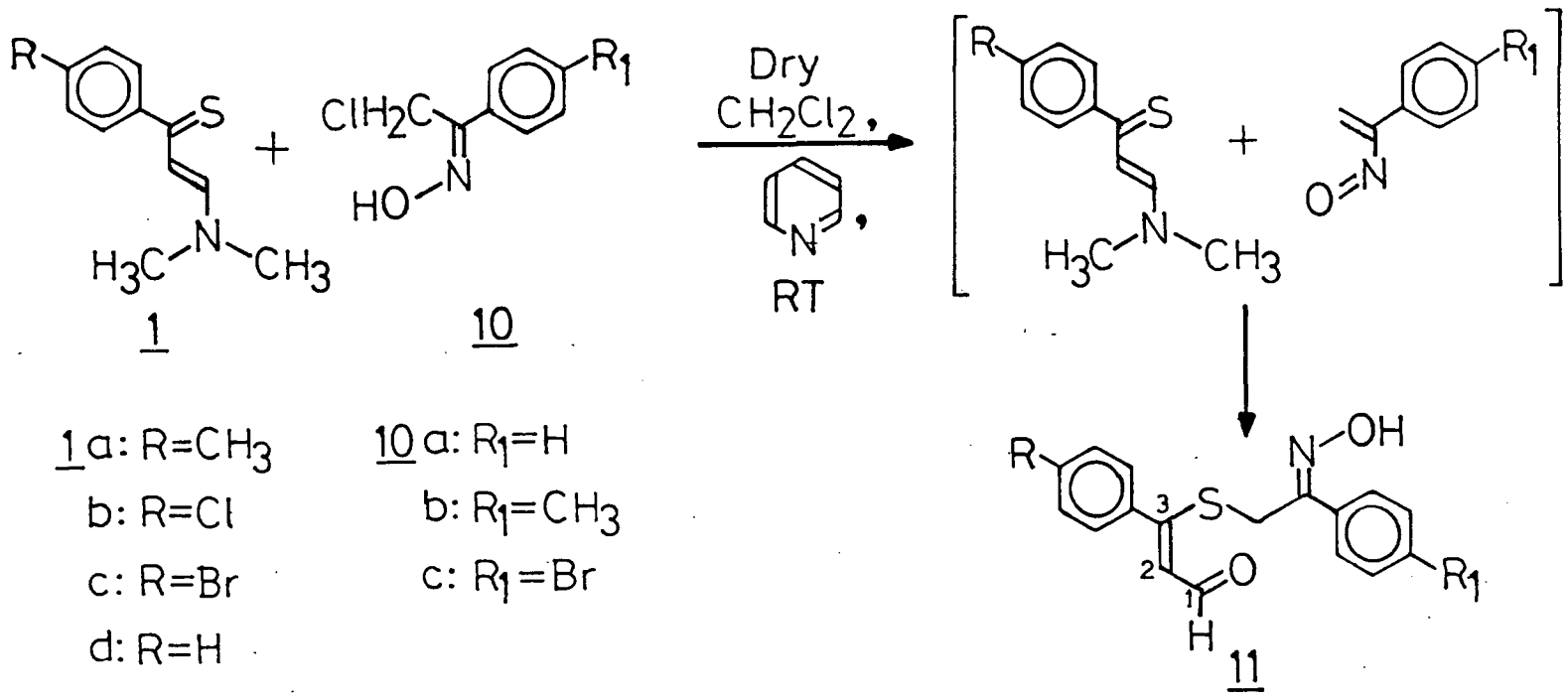
of thiopyran derivative 7 to its epimer 8 probably takes place by initial opening of 7 to give the intermediate 9 followed by ring closure leading to thermodynamically more stable thiopyran derivative 8.

3.2.2 Reactions of thioamide vinylogs with Nitrosoalkenes:

Treatment of 3-dimethylamino-1-arylpropene-1-thione (1) with an equivalent amount of α-halogeno oxime (10), in the presence of 1.2 equivalent pyridine, in dry dichloromethane at room temperature resulted in 50-75% yields of

products (11). These products have been identified as 3-aryl-3(2-aryl-2-oximinoethylthio)-prop-2-enal (11) (Scheme 5). The product 11a, for example, analysed for $C_{18}H_{17}NOS$. Its mass spectrum exhibited weak (2%) molecular ion peak at m/z 311(M^+) while the base peak at m/z 177(M^+-134) is assigned to the fragment $[H_3C-C_6H_4-C(=S)-CH-C(=O)-H]^+$ formed probably by the loss of ion($H_2C-C(=NOH)-C_6H_5$) from the molecular ion. The IR spectrum (KBr) of 11a showed strong absorption peaks at 3200 and 1620 cm^{-1} assigned respectively to imino and aldehydic carbonyl stretchings. Its ^1H NMR spectrum ($CDCl_3$) exhibited two singlets at δ 2.33(3H) and 4.15(2H) assigned to three methyl protons (H_3C-C$_6$H$_4$-) and two methylene protons ($-CH_2-$) respectively. The presence of one doublet at δ 6.27 (J=8Hz) could be due to vinylic proton. The nine aromatic protons appeared as a multiplet in the region δ 7.06-7.51 and the aldehydic proton appeared as a doublet at δ 9.24. Finally the broad peak at δ 9.45, exchangeable with D_2O, is assigned to the OH proton of the oximino functional group.

Further structural proof for 11a was obtained from its ^{13}C NMR spectral assignments made on the basis of off resonance decoupled spectrum. It showed the peaks at δ 21.32(H_3C-C$_6$H$_4$-), 27.01(C-5), 190.31(C-1), 167.46 (C-6), 152.82(C-3), 140.87(C-8), 134.17(C-9 or C-7),

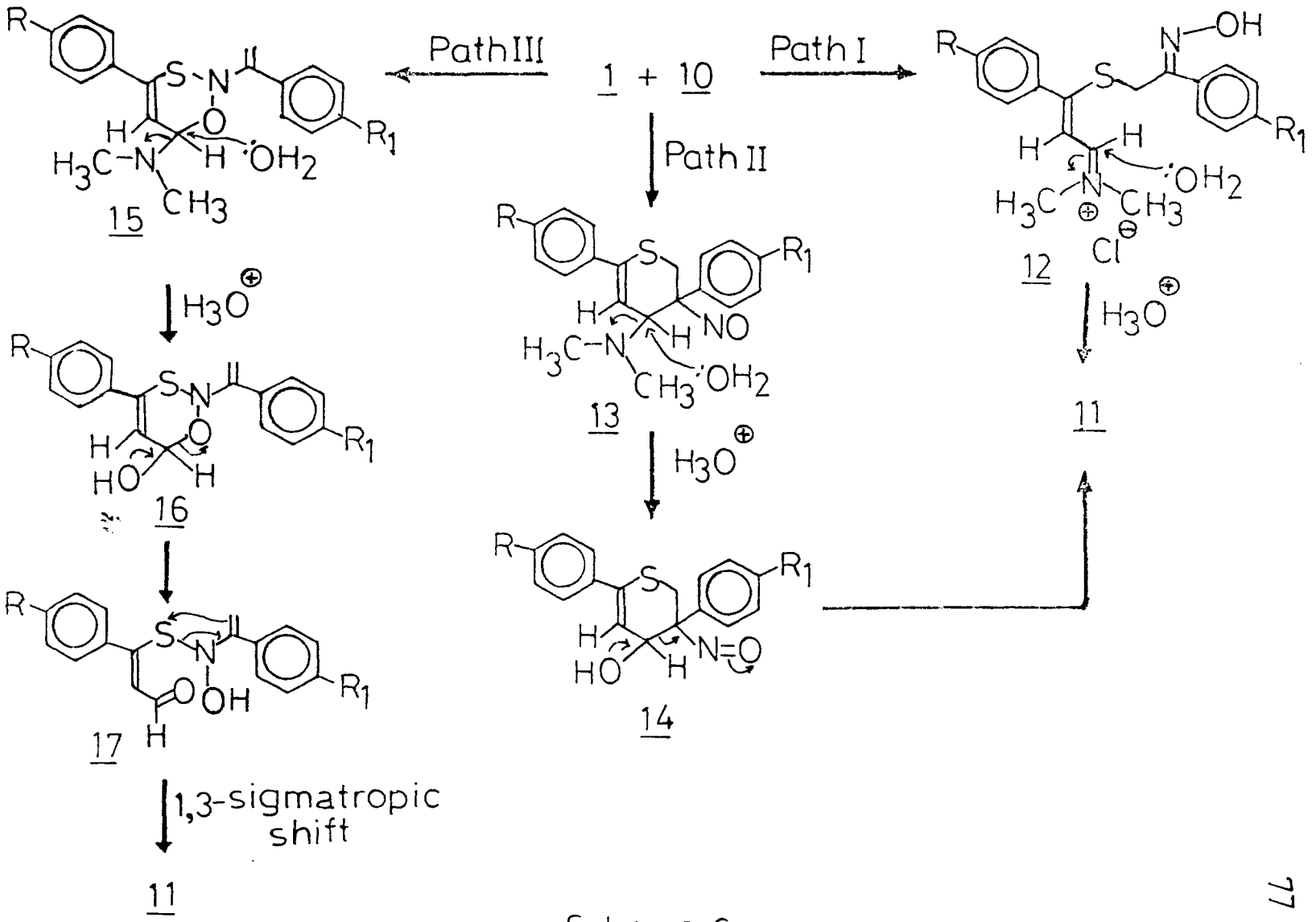


1 a: R=CH_3
b: R=Cl
c: R=Br
d: R=H

10 a: R_1=H
b: R_1=CH_3
c: R_1=Br

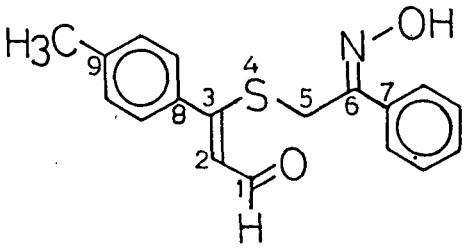
11 a: R=CH_3, R_1=H
b: R=R_1=CH_3
c: R=CH_3, R_1=Br
d: R=Cl, R_1=H
e: R=Cl, R_1=CH_3
f: R=Cl, R_1=Br
g: R=Br, R_1=H
h: R=R_1=H
i: R=H, R_1=CH_3
j: R=H, R_1=Br

Scheme 5


Path III
1 + 10
Path I
Path II
15
12
13
11
16
17
14
$H_3O^{\oplus}$
1,3-sigmatropic shift

Scheme 6

131.82(C-7 or C-9) and 123.32(C-2). Other aromatic carbons are observed at δ126.48, 128.52, 128.67, 129.66, 129.28, 129.48, 130.25 and 130.36.



11a

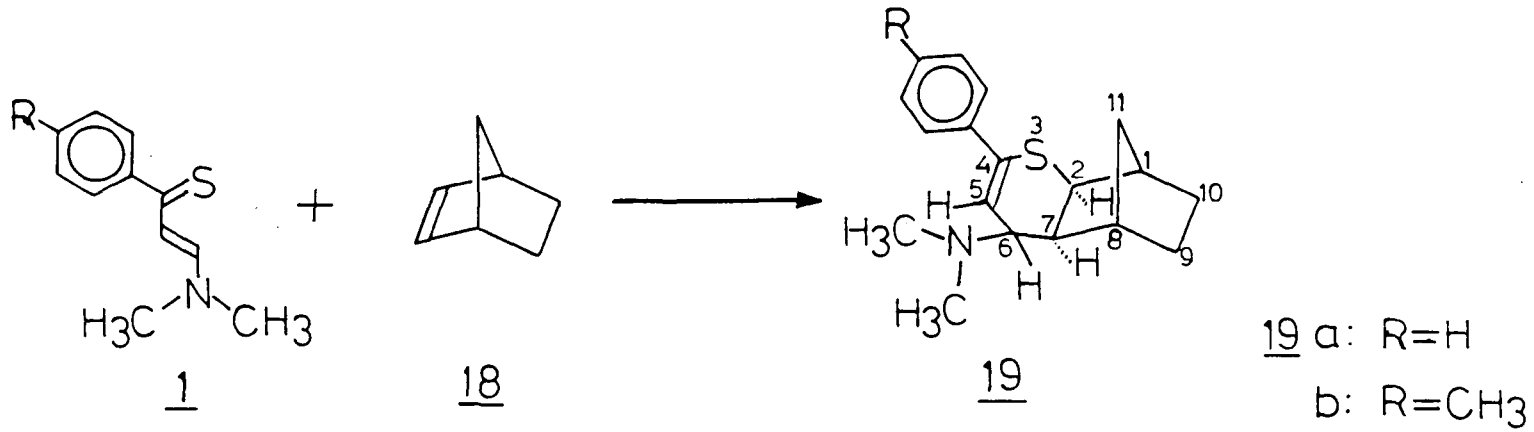
The three probable mechanistic pathways leading to the formation of 11 are outlined in Scheme 6. In the pathway I it is assumed that the initial nucleophilic attack of the sulphur of thioamide vinylog at the methylene bearing the leaving group chlorine results in the iminium salt intermediate 12 and its hydrolytic decomposition results in product 11. The pathway II assumes the formation of initial (4+2) adduct (13) formed by the 2π participation of C=C of vinylnitroso compound. This is less likely since in most of the known cycloadditions of vinylnitroso compounds the N=O is known to participate as 2π component. The pathway III leads initially to (4+2) cycloadduct 15 formed by the 2π participation of N=O of vinylnitroso compound. This cycloadduct undergoes hydrolytic decomposition leading to 17 via oxathiazine derivative 16.

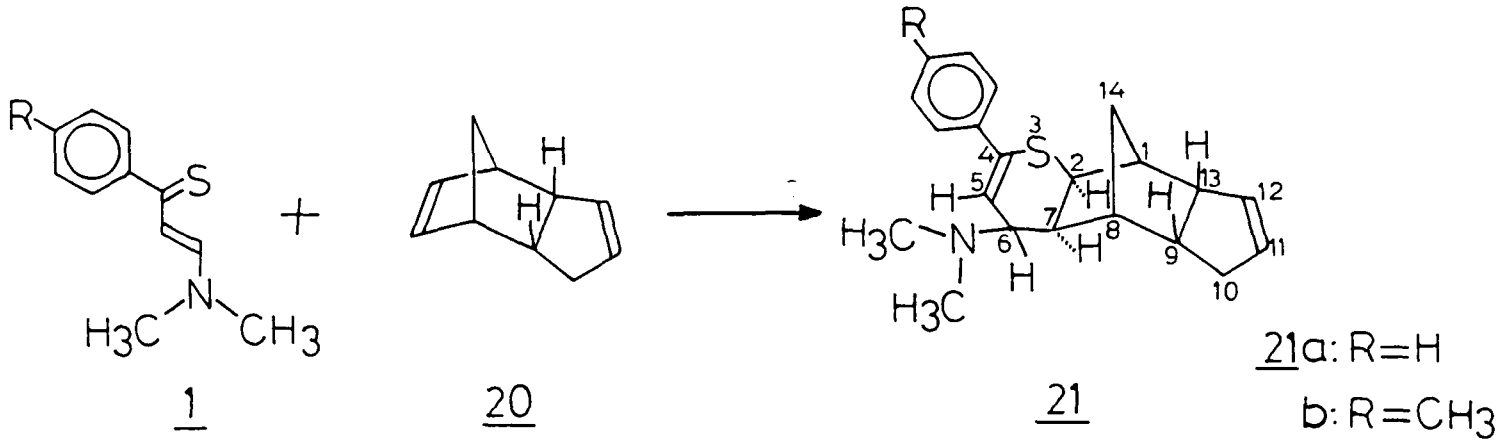
The compound 17 subsequently undergoes [1,3] sigmatropic shift resulting in the product 11. The precise mechanism followed in these reactions is still being investigated.

3.2.3 Reactions of thioamide vinylogs with norbornylene and dicyclopentadiene:

The treatment of 3-dimethylamino-1-arylpropene-1-thiones (1) with norbornylene (18) in refluxing benzene resulted in Diels-Alder adducts 19 characterized as exo-4-aryl-6-dimethylamino-3-thiatricyclo [6.2.1.$0^{2,7}$] undeca-4-ene on the basis of analytical and spectral evidences. The compound 19a analysed for $C_{18}H_{23}NS$ and its mass spectrum showed the molecular ion peak at m/z 285(4) (m^+). Other important peaks are observed at m/z 241(4)(m^+-$N(CH_3)_2$), 191(32)(m^+-norbornylene) and 158(m^+-norbornylene-SH). The ^1H NMR spectrum of 19a showed multiplets spread in the region δ1.10-2.60(9H) assigned to six protons of three methylene groups, two bridgehead protons (H_1 and H_8) and H_7 proton. The singlet at δ 2.36(6H) is assigned to $N(CH_3)_2$ protons. The protons H_2 and H_6 appeared as dd at δ 3.06($J_{H_{1,2}}$=2Hz, $J_{H_{2,7}}$=8Hz) and δ 3.02($J_{H_{6,7}}$=8Hz, $J_{H_{5,6}}$=4Hz) respectively. The doublet at δ 6.58($J_{H_{5,6}}$=4Hz) is assigned to the vinylic proton H_5 and the five aromatic protons appeared as a multiplet in the region δ 7.23-7.67. Although it is difficult to assign signals due to H_7 and various other protons still the appearance of a dd at

δ 3.06 with coupling constants of 8.0 Hz and 2Hz indicate that the coupling constant between H_2 and H_7 is 8.0 Hz. This value indicates cis configuration for the fusion of thiopyran and norbornane moieties. The ^{13}C NMR spectra of 2-substituted norbornanes have been well studied[16]. It has been reported that the exo-2 gp usually shields C-11 (the resonance of C-11 is upfield 1.3-4.4 ppm) while the endo counterpart shields C-10(the resonance of C-10 is upfield by 4.9-9.7 ppm from the one in norbornane)[16]. Hence the final proof about the structure of 19a was obtained from its ^{13}C NMR spectrum. The noise decoupled ^{13}C spectrum of 19a showed C-9 and C-10 as triplets at δ 29.13 and 29.93 respectively. The pair of doublets because of the two protons with widely separated chemical shifts are attributed to the C-11 absorption at δ34.41. In addition it showed peaks at δ 41.04 (C-1 or C-8), 41.92($N(CH_3)_2$), 43.39(C-8 or C-1), 51.17(C-7), 52.87 (C-2), 66.60(C-6), 123.63(C-5) and 139.38(C-4). Other phenyl carbons are observed at δ 123.64, 126.17, 128.36 and 128.77. Thus the C-11 resonance is shifted upfield by 5.09 ppm and those of C-9 and C-10 are shifted upfield by 0.95 and 0.49 compared to those of norbornane . These values probably indicate exo-cis configuration for 19 (Scheme 7).

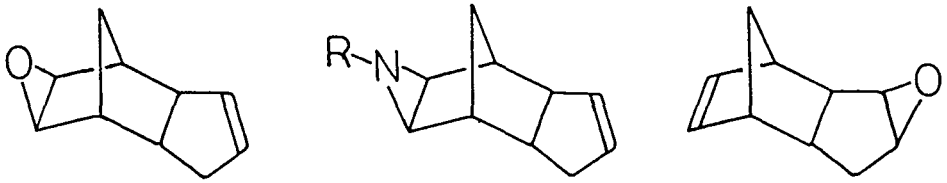

R
S
N
H3C
CH3
1
18
19
19 a: R=H
b: R=CH3
c: R=Cl


R
S
N
H3C
CH3
1
20
21
21a: R=H
b: R=CH3
c: R=Cl
d: R=Br

Scheme 7

Similarly the reactions of 3-dimethylamino-1-arylpropene-1-thiones (1) with dicyclopentadiene (4,7-methano-3a,4,7,7a-tetrahydro-1H-indene)(20) resulted in regiospecific addition of thioamide vinylogs across 5,6-double bond of 4,7-methano-3a,4,7,7a-tetrahydro-1H-indene(20). The products so obtained have been characterized as exo-4-aryl-6-dimethylamino-3-thiatetracyclo $[5.5.1.0^{2,7}, 0^{9,13}]$ tetradeca-4,11-diene (21) on the basis of analytical and spectral data and on the basis of literature evidences concerning the dicyclopentadiene adducts. Thus the compound 21a analysed for $C_{21}H_{25}NS$ and its mass spectrum exhibited the molecular ion peak at m/z 323(M^+). The base peak at m/z 191(100%) is assigned to the fragment $[C_6H_5-\overset{S}{\overset{\|}{C}}-CH=CH-N(CH_3)_2]^+$ obtained by the loss of dicyclopentadiene fragment. Its ^1H NMR spectrum showed a multiplet in the region δ1.48-1.90(2H), multiplet in the region δ2.12- 2.34(3H), a singlet at δ2.38(6H), multiplet in the region δ2.50- 2.70(3H), multiplet in the region δ 3.00- 3.24(3H), multiplet in the region δ 5.50- 5.68(2H), a doublet at 6.51(1H, J=4Hz) and a multiplet at δ7.17- 7.57(5H). Of these the multiplet at δ 3.00- 3.24(3H) is assigned to the protons H_2,H_6 and H_7 while the multiplet at δ5.50- 5.68 and the doublet at δ 6.51($J_{H_5H_6}$=4Hz) are assigned to the vinylic protons H_{11},H_{12} and H_5 respectively. The formation of exo adducts across 5,6-double bond of 1H-indene(20)

is preferred over the formation of exo adducts across 2,3-double bond of 1H indene (20)[17-19]. This may be due to higher strain across 5,6-double bond over 2,3-double bond. Also, it has been reported that in case of the epoxide A[17] and aziridine B[18] the two vinylic protons appear as multiplet around δ 5.60 while the vinylic protons in case of epoxide C have been reported to appear as a multiplet around δ 6.0[17]. Hence it may



A B C

be concluded that the cycloadducts formed in case of reactions of 1 with 20 may have the structure 21 as indicated in the Scheme 7. The same products 21 are obtained on heating a solution of 1 and freshly distilled cyclopentadiene in dry benzene in a sealed tube for 8 hours.

3.3 EXPERIMENTAL SECTION:

General conditions are same as described in chapter II.

Starting materials:

The commercial samples of acetophenone, 4-chloroacetophenone, 4-bromoacetophenone, 4-methylacetophenone, chloroacetyl chloride, carbondisulphide, benzaldehyde, p-anisaldehyde,

2-furaldehyde, nitromethane, N,N-dimethylformamide and dimethyl sulphate were purified before use.

W-Chloroacetophenone, m.p. 56-57°C[20]: W-chloro-4-methyl-acetophenone, m.p. 67°C[21]: W-chloro-4-bromoacetophenone, m.p. 116-117°C [22]: W-chloro-4-chloroacetophenone, m.p. 101-102°C[23]: ß-nitrostyrene, m.p.56-58°C[24]: ß-nitro-p-methoxystyrene, m.p. 87°C[25] and ß-nitro-α-(α-furyl)-ethylene , m.p. 74-75°C[26] were prepared by the reported procedures.

3-Dimethylamino-1-phenylpropene-1-one, m.p. 96-98°C[27]: 3-dimethylamino-1-(4-chlorophenyl)propene-1-one, m.p.84-86°C[27]; 3-dimethylamino-1-(4-methylphenyl)propene-1-one, m.p.95°C (lit. 95-96°C)[27]: 3-dimethylamino-1-(4-bromophenyl) propene-1-one: m.p. 75-77°C[27]: 3-dimethylamino-1-phenyl-propene-1-thione, m.p. 115-116°C[27]: 3-dimethylamino-1-(4-chlorophenyl)propene-1-thione, m.p.119-120°C[27]; 3-dimethyl-amino-1-(4-methylphenyl)propene-1-thione, m.p.135-136°C[27]; 3-dimethylamino-1-(4-bromophenyl)propene-1-thione, m.p. 118-119°C[27]; 3-anilino-1-phenylpropene-1-thione, m.p. 102°C(lit.[28] 105-106°C): 3-p-toludino-1-phenylpropene-1-thione, m.p. 140°C(lit.[29] m.p. 142-145°C): and 3-p-chloro-phenylamino-1-phenylpropene-1-thione, m.p. 129°C were prepared as detailed in chapter II, by following the reported procedures.

Preparation of w-chloroacetophenone oxime[30]:

A homogeneous solution of w-chloroacetophenone (1 mol) and hydroxylammonium chloride (3 mol) was prepared in small amount of methanol containing minimum amount of water. The solution was allowed to stand overnight at room temperature. The dilution of the solution with water yielded w-chloroacetophenone oxime, which was recrystallised from carbon tetrachloride, m.p. 88-89°C[30].

W-chloro-4-chloroacetophenone oxime, m.p. 101°C[23]: w-chloro-4-bromoacetophenone oxime, m.p. 115°C[22]: w-chloro-4-methylacetophenone, m.p. 87-88°C were prepared by following the same procedure.

General procedure for the preparation of (2S,3R,4R)-6-aryl-(2)-aryl/furyl-3,4-dihydro-(4)-dimethylamino-(3)-nitro-2H-thiopyran (4a-4i):

The solution of a mixture of 3-dimethylamino-1-p-tolylpropene-1-thione (1a) (1.0g, 0.0048 mol) and ß-nitrostyrene (3a) (715 mg: 0.0048 mol) in dry dichloromethane (20 ml) was stirred at room temperature for 20 minutes. The solvent was removed under reduced pressure and the product 4a thus obtained (1.6g: 93%) was recrystallised from benzene, m.p. 140°C (Found: C,68.27: H,6.45: N,7.90, $C_{20}H_{22}N_2O_2S$ requires: C,67.80: H,6.21: N,7.91%). IR spectrum (KBr) ν_{max}: 1545(NO_2), MS: m/z 205(M^+-149), 149(M^+-205). ^1H NMR spectrum ($CDCl_3$) δ ppm: 2.33(s,3H,

H_3C-Ph), 2.66(s,6H,$N(CH_3)_2$), 4.26(dd,1H,H_4,$J_{H_3H_4}$ = ~11Hz & $J_{H_4H_5}$ = ~3Hz), 4.79(d,1H,H_2,$J_{H_2H_3}$ = ~11Hz), 5.26(dd,1H, H_3,$J_{H_2H_3}$ =11Hz & $J_{H_3H_4}$ = ~11Hz), 6.00(d,1H,H_5,$J_{H_4H_5}$ = ~3Hz), 7.06-7.40(m,9H,Ar-H).

The same procedure was followed for the preparation of all other (2S,3R,4R)-6-aryl-2-aryl/furyl-3,4-dihydro-(4)-dimethylamino-(3)-nitro-2H-thiopyrans (4b-4i)(Tables 1 and 2).

General procedure for the preparation of 6-aryl-2-aryl/furyl-3-nitro-2H-thiopyrans (5a-5i):

A solution of compound 4a (1.0g: 0.0028 mol) in dichloromethane (20 ml) and acetic acid (2 ml) was stirred at room temperature for one hour. The reaction mixture was then washed with a saturated solution of sodium bicarbonate, water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue so obtained was chromatographed over silica gel column. Elution of the column with hexane gave 3-nitro-6-(4-methylphenyl)-2-phenyl-2H-thiopyran 5a (0.7g: 80%), recrystallised from petrolium ether, m.p. 108°C. IR spectrum ν_{max}(KBr): 1625, 1500, 1300 cm^{-1}. (Found: C,70.26: H,4.99: N,4.60: Mol. wt. 309, (mass spectrometry): $C_{18}H_{15}NOS$ requires: C,69.90: H,4.85: N,4.53%): Mol. wt. 309. δ_H ppm ($CDCl_3$): 2.36(s,3H, CH_3-Ph): 5.69(s,1H,H_2), 6.63(d,1H,H_5,J=7-8Hz), 7.13-7.50(m,9H,Ar-H), 8.00(d,1H, H_4,$J_{4',5}$=7-8Hz).

All other 6-aryl-2-aryl/furyl-3-nitro-2H-thiopyrans (5a-5i) were prepared by following the same procedure (Table 1 and 2).

General procedure for the reactions of 3-arylamino-1-phenylpropene-1-thione (2) with nitroalkenes (3): Preparation of (2S,3R,4S)-(2)-aryl-(4)-arylamino-(3)-nitro-6-phenyl-3,4-dihydro-2H-thiopyrans (7a-7e):

A mixture of 3-p-toluidino-1-phenylpropene-1-thione(2a) (1.0g; 0.0039 mol) and ß-nitrostyrene (3a) (0.6g, 0.004 mol) was dissolved in dry benzene (25 ml) and the reaction mixture was stirred at room temperature for 20 minutes. The solvent was removed under reduced pressure and the solid so obtained (7a) (1.2g; 75%) was recrystallised from a mixture (1:1) of benzene and hexane, m.p.116^{o}C. IR spectrum (KBr) ν_{max}: 3400($_{N-H}$), 1610 ($\nu_{C=C}$), 1545 (ν_{NO_2}) cm^{-1}. (Found: C,72.08: H,5.59: N,7.06: Calcd for $C_{24}H_{22}N_2O_2S$: C,71.64: H,5.47: N,6.96%). Mass spectrometry: m/z 149 (m^+-253), 253(m^+-149). δ_H ppm ($CDCl_3$): 2.20(s,3H,H_3C-Ph), 3.76(bd,1H,NH), 4.80(dd,1H,H_4,$J_{3,4}$= 4Hz, $J_{4,5}$=6Hz), 5.00(d,H_2,$J_{2,3}$=11Hz), 5.36(dd,H_3,$J_{2,3}$= 11Hz, $J_{3,4}$=4Hz), 6.18(d,H_5,$J_{4,5}$=6Hz), 6.50(d,2H,H_a), 6.96 (d,2H,H_b,$J_{a,b}$=8Hz), 7.13-7.60(m,10H,aromatic).

Similar procedure was followed for the preparation of all other derivatives of 7 (7b-7e) (Tables 3 and 4).

Conversion of (2S,3R,4S)-(2)-aryl-(4)-arylamino-(3)-nitro-6-phenyl-3,4-dihydro-2H-thiopyrans (7) to (2S,3R,4R)-(2)-aryl-(4)-arylamino-(3)-nitro-6-phenyl-3,4-dihydro-2H-thiopyrans (8): A General Procedure:

A solution of compound 7a (0.5g: 0.0012 mol) in benzene (20 ml) was treated with glacial acetic acid (1 ml) and the reaction mixture was stirred at room temperature for five hours. The reaction mixture was then washed with saturated sodium bicarbonate solution, water and dried over anhydrous sodium sulphate. The removal of the solvent under reduced pressure resulted in 8a (0.4g: 80%) which was recrystallised from benzene, m.p. 128°C. IR spectrum (KBr) ν_{max}: 3400 (ν_{N-H}), 1610($\nu_{C=C}$), 1550(ν_{NO_2}) cm^{-1}, (Found: C,72.18: H,5.63: N,6.80: Mol. wt. 402 (mass spectrometry). Calcd. for $C_{24}H_{22}N_2O_2S$: C,71.64: H,5.47: N,6.96%: Mol. wt.402). δ_H ppm($CDCl_3$): 2.23(s,3H,H_3C-Ph), 3.63(bd,1H,NH), 4.95(d,H_2,$J_{2,3}$=11Hz), 5.09(dd,1H,H_4,$J_{3,4}$ = 11Hz: $J_{4,5}$=3Hz), 5.31(dd,1H,H_3,$J_{2,3}$= $J_{3,4}$=11Hz), 6.03 (d,1H,H_5,$J_{4,5}$=3Hz), 6.63(d,2H,H_a), 7.02(d,2H,H_b,$J_{a,b}$=8Hz), 7.13-7.53(m,10H,Ar-H).

All other compounds 8b-8i were prepared by following the same procedure (Tables 3 & 4). The compounds 8 were also obtained in good yields by

(i) By refluxing equimolar mixture of 2 and 3 in dry acetonitrile for 5 hours.

(ii) By refluxing a solution of compounds 7 in dry benzene for 10 hours.

General procedure for the reactions of thioamide vinylogs(1) with nitrosoalkenes. Preparation of 3-aryl-3-(2-aryl-2-oximinoethylthio)-prop-2-enal(11):

The solution of a mixture of 3-dimethylamino-1-(4-methyl-phenyl)propene-1-thione(1a) (0.9g: 0.0042 mol), ω-chloroacetophenone oxime (10a) (0.8g: 0.0047 mol) and pyridine (0.4g) in dry dichloromethane (25 ml) was stirred at room temperature for 30 hours. The reaction mixture was washed with water, saturated sodium bicarbonate solution, again with water and dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue obtained was chromatographed over silica gel column. Elution of the column with a mixture (1:1) of benzene and hexane gave 11a (0.9g: 66%) which was recrystallised from a mixture (1:1) of benzene and hexane, m.p. 141°C. IR spectrum (KBr) ν_{max}: 3200($\nu_{C=N-OH}$), 1620 ($\nu_{C=N}$). (Found: C,69.61: H,5.32: N,4.38: Mol.wt. 311(mass spectrometry). Calcd. for $C_{18}H_{17}NO_2S$: C,69.45: H,5.47: N,4.50%: Mol. wt. 311). δH ppm ($CDCl_3$): 2.33(s,3H,CH_3-Ph), 4.15 (s,2H,-CH_2-), 6.27(d,1H,=C-H: J=8Hz), 7.06-7.51(m,9H, aromatic), 9.24(d,1H,C-H), 9,45(b,1H,=N-OH: exchangeable with D_2O).

The reactions of all other 3-dimethylamino-1-arylpropene-1-thiones (1) with nitrosoalkenes generated in situ from

w-chloro oximes (10) were carried out by following the same procedure. The physical, analytical and spectral data for 11b-11j are listed in Tables 5 and 6.

Reactions of thioamide vinylogs (1) with norbornylene(18): Preparation of exo-4-aryl-6-dimethylamino-3-thiatricyclo [6.2.1.$0^{2,7}$] undeca-4-ene(19): A general procedure:
A solution of 3-dimethylamino-1-phenylpropene-1-thione (1.0g: 0.0052 mol) and norbornylene (0.6g: 0.0064 mol) in dry benzene (20 ml) was refluxed for 48 hours. The solvent was removed under reduced pressure and the residue so obtained was chromatographed over silica gel. Elution of the column with a mixture (1:19) of ethyl acetate and hexane gave 19a (1.3g: 87%) which was recrystallised from hexane, m.p.75°C. IR (KBr) ν_{max}: 1595, 1580,1475, 1445 cm^{-1}. (Found: C,75.61: H,8.17: N,4.96: Mol.wt. 285(mass spectrometry). Calcd. for $C_{18}H_{23}NS$: C,75.79: H,8.07: N,4.91%; Mol. wt. 285). δH ppm($CDCl_3$): 1.10-2.60(m,9H), 2.36(s,6H,$-N(CH_3)_2$), 3.02(dd,1H,H_6, $J_{6,7}$=8Hz and $J_{5,6}$=4Hz), 3.06(dd,1H,H_2,$J_{1,2}$=2Hz and $J_{2,7}$=8Hz), 6.58(d,1H,H_5,$J_{5,6}$=4Hz), 7.23-7.67(m,5H,Ar-H). δC ppm($CDCl_3$): 29.13(C-9), 29.93(C-10), 34.41(C-11), 41.04(C-1/C-8), 41.92($N(CH_3)_2$), 43.39(C-8/C-1), 51.17 (C-7), 52.87(C-2), 66.60(C-6), 123.63(C-5), 139.38(C-4), 123.64, 126.17, 128.36, 128.77(Ar).

The compounds 19b and 19c were also prepared by the same procedure and their physical, analytical and spectral data are listed in Tables 7 and 8.

General procedure for the reactions of thioamide vinyloes(1) with dicyclopentadiene (20): Preparation of exo-4-aryl-6-dimethylamino-3-thiatetracyclo ($6.5.1.0^{2,7}$, $0^{9,13}$) tetradeca-4-11,diene(21):

A solution of 3-dimethylamino-1-phenylpropene-1-thione (1.0g; 0.0052 mol) and dicyclopentadiene (0.8g; 0.0060 mol) in dry benzene (25 ml) was refluxed for thirty hours. Solvent was removed under reduced pressure and the residue was chromatographed over silica gel. Elution of the column with a mixture (1:19) of ethyl acetate and hexane gave the product 21a (65%) which was recrystallised from hexane, m.p.71°C. (Found: C,78.61: H,7.50: N,4.08. Mol. wt. 323(mass spectrometry). Calcd. for $C_{21}H_{25}NS$: C,78.02: H,7.74: N,4.33%: mol. wt.323). δ_H ppm($CDCl_3$): 1.48-1.90 (m,2H), 2.12-2.34(m,3H), 2.38(s,6H,$-CH_3)_2$. 2.50-2.70(m, 3H), 3.00-3.24(m,3H), 5.58-5.68(m,2H,H_{11} and H_{12}), 6.51 (d,1H,H_5,$J_{5.6}$=4Hz), 7.17-7.57(m,5H,Ar-H).

The cycloadducts 21b-21d were prepared by following the same procedure (Tables 7 and 8).

Table 1: Physical and analytical data for compounds 4a-4i and 5a-5i

Compounds	R	R_1	m.p. °C	Yield %	Mol. formula	Calc. / Found	Analysis % C	H	N	M/z
4a	CH_3	C_6H_5	140	93	$C_{20}H_{22}N_2O_2S$ (354)	Calc.	67.80	6.21	7.91	205 (M^+-149)
						Found	68.27	6.45	7.90	149 (M^+-205)
4b	CH_3	p-$OMeC_6H_4$	114	94	$C_{21}H_{24}N_2O_3S$ (384)	Calc.	65.63	6.25	7.29	205 (M^+-179)
						Found	66.12	6.01	7.11	179 (M^+-205)
4c	CH_3		101	78	$C_{18}H_{20}N_2O_3S$ (344)	Calc.	62.79	5.81	8.14	
						Found	63.09	6.14	8.09	
4d	Cl	C_6H_5	118	90	$C_{19}H_{19}ClN_2O_2S$ (374.5)	Calc.	60.88	5.07	7.48	
						Found	61.32	4.97	7.22	
4e	Cl	p-$OMeC_6H_4$	132	92	$C_{20}H_{21}N_2ClO_3S$ (404.5)	Calc.	59.33	5.19	6.92	
						Found	60.05	5.12	6.51	
4f	Cl		95	81	$C_{17}H_{17}ClN_2O_3S$ (364.5)	Calc.	55.97	4.66	7.68	
						Found	56.35	5.05	7.55	
4g	H	C_6H_5	146	92	$C_{19}H_{20}N_2O_2S$ (340)	Calc.	67.06	5.88	8.23	191 (M^+-149)
						Found	67.52	5.67	7.92	149 (M^+-191)
4h	H	p-$OMeC_6H_4$	131	93	$C_{20}H_{22}N_2O_3S$ (370)	Calc.	64.86	5.94	7.57	
						Found	65.45	6.27	7.54	
4i	H		104	80	$C_{17}H_{18}N_2O_3S$ (330)	Calc.	61.82	5.45	8.48	
						Found	61.98	5.52	8.37	

Table 1. Contd....

Compounds	R	R_1	m.p. °C	Yield %	Mol.formula	Calc. Found	Analysis % C	H	N	M/z
5a	CH_3	C_6H_5	108	80	$C_{18}H_{15}NO_2S$		69.90 70.26	4.85 4.99	4.53 4.60	309 (M^+)
5b	CH_3	p-$OMeC_6H_4$	95	75	$C_{19}H_{17}NO_3S$		67.25 68.05	5.01 4.96	4.13 4.02	339 (M^+)
5c	CH_3		80	69	$C_{16}H_{13}NO_3S$		64.21 65.07	4.35 4.25	4.68 4.56	299 (M^+)
5d	Cl	C_6H_5	170	78	$C_{17}H_{12}ClNO_2S$		61.91 62.33	3.64 3.57	4.25 4.16	329 (M^+)
5e	Cl	p-$OMeC_6H_4$	70	76	$C_{18}H_{14}ClNO_3S$		60.08 60.63	3.89 3.84	3.89 3.78	359 (M^+)
5f	Cl		114	70	$C_{15}H_{10}ClNO_3S$		56.34 57.08	3.13 3.07	4.38 4.33	319 (M^+)
5g	H	C_6H_5	85	81	$C_{17}H_{13}NO_2S$		69.15 69.73	4.41 4.55	4.74 4.90	295 (M^+)
5h	H	p-$OMeC_6H_4$	63	79	$C_{18}H_{15}NO_3S$		66.46 67.03	4.62 4.60	4.31 4.29	325 (M^+)
5i	H		65	65	$C_{15}H_{11}NO_3S$		63.16 64.00	3.86 3.85	4.91 4.83	285 (M^+)

Table 2: Spectral data for compounds 4a - 4i and 5a - 5i

Compounds	R	R_1	IR(KBr) ν_{max} cm^{-1}	^1H NMR($CDCl_3$) δ ppm
4a	CH_3	C_6H_5	1600,1545,1300	2.33(s,3H,H_3C-Ph), 2.66 (s,6H,$N(CH_3)_2$), 4.26(dd, 1H,H_4,$J_{H_3H_4}$=11Hz & $J_{H_4H_5}$= 3Hz), 4.79(d,1H,H_2,$J_{H_2H_3}$= 11Hz), 5.26(dd,1H,H_3,$J_{H_2H_3}$= 11Hz & $J_{H_3H_4}$=11Hz), 6.00 (d,1H,H_5,$J_{H_4H_5}$=3Hz), 7.06-7.40(m,9H,Ar-H)
4b	CH_3	p-$OMeC_6H_4$	1610,1545,1300	2.33(s,3H,CH_3-Ph), 2.46(s, 6H,$N(CH_3)_2$), 3.76(s,3H, OCH_3), 4.23(dd,1H,H_4, $J_{H_3H_4}$=11Hz & $J_{H_4H_5}$=3Hz), 4.73(d,1H,H_2,$J_{H_2H_3}$=11Hz), 5.17(dd,1H,H_3,$J_{H_2H_3}$=11Hz & $J_{H_3H_4}$=11Hz), 5.92(d,1H,H_5, $J_{H_4H_5}$=3Hz), 6.72-7.30(m, 8H,Ar-H)

Table 2: Contd....

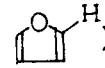
Compounds	R	R_1	IR(KBr) ν_{max} cm^{-1}	^1H NMR($CDCl_3$) δ ppm
4c	CH_3		1620,1600,1500, 1310	2.43(s,3H,CH_3-Ph), 2.53 (s,6H,$N(CH_3)_2$), 4.26(dd, 1H,H_4,$J_{H_3H_4}$=11Hz & $J_{H_4H_5}$= 3Hz), 4.90(d,1H,H_2,$J_{H_2H_3}$= 11Hz), 5.23(dd,1H,H_3,$J_{H_2H_3}$= 11Hz & $J_{H_3H_4}$=11Hz), 6.00 (d,1H,H_5,$J_{H_4H_5}$=3Hz), 6.30-6.66(m,2H, ), 7.00-7.80(m,5H,Ar-H & )
4d	Cl	C_6H_5	1600,1555,1310	2.43(s,6H,$N(CH_3)_2$), 4.26(dd, 1H,H_4,$J_{H_3H_4}$=11Hz & $J_{H_4H_5}$= 3Hz), 4.76(d,1H,H_2,$J_{H_2H_3}$= 11Hz), 5.19(dd,1H,H_3,$J_{H_2H_3}$= 11Hz & $J_{H_3H_4}$=11Hz), 6.00 (d,1H,H_5,$J_{H_4H_5}$=3Hz), 7.2-7.4(m,9H,Ar-H)

Table 2: Contd...

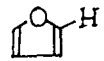
Compounds	R	R_1	IR(KBr) ν_{max} cm^{-1}	^1H NMR($CDCl_3$) δ ppm
4e	Cl	p-$OMeC_6H_4$	1620,1550,1300	2.43(s,6H,$N(CH_3)_2$), 3.76(s,3H, OCH_3), 4.23(dd,1H,H_4,$J_{H_3H_4}$= 11Hz & $J_{H_4H_5}$=3Hz), 4.73(d,1H, H_2,$J_{H_2H_3}$=11Hz), 5.17(dd,1H, H_3,$J_{H_2H_3}$=11Hz & $J_{H_3H_4}$=11Hz), 5.92(d,1H,H_5,$J_{H_4H_5}$=3Hz), 6.72-7.30(m,8H,Ar-H)
4f	Cl		1600,1550,1310	2.43(s,6H,$N(CH_3)_2$), 4.27(dd,1H, H_4,$J_{H_3H_4}$=11Hz & $J_{H_4H_5}$=3Hz), 5.10(d,1H,H_2,$J_{H_2H_3}$=11Hz),5.36 (dd,1H,H_3,$J_{H_2H_3}$=11Hz & $J_{H_3H_4}$= 11Hz). 6.03(d,1H,H_5,$J_{H_4H_5}$=3Hz), 6.2-6.7(m,2H, ), 7.20-7.90(m,5H,Ar-H & ).
4g	H	C_6H_5	1600,1540,1300	2.45(s,6H,$N(CH_3)_2$,4.30(dd,1H, H_4,$J_{H_3H_4}$=11Hz & $J_{H_4H_5}$=3Hz), 4.85(d,1H,H_2,$J_{H_2H_3}$=11Hz),

Table 2: Contd....

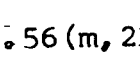
Compounds	R	R_1	IR(KBr) $\nu_{max}cm^{-1}$	^1H NMR($CDCl_3$) δppm
				5.30(dd,1H,H_3,$J_{H_2H_3}$=11Hz & $J_{H_3H_4}$=11Hz), 6.03(d,1H,H_5, $J_{H_4H_5}$=3Hz), 7.21-7.50(m,10H, Ar-H)
4h	H	p-$OMeC_6H_4$	1610,1550,1305	2.40(s,6H,$N(CH_3)_2$, 3.69(s,3H, OCH_3), 4.17(dd,1H,H_4,$J_{H_3H_4}$= 11Hz & $J_{H_4H_5}$=3Hz), 4.66(d, 1H,H_2,$J_{H_2H_3}$=11Hz), 5.13(dd, 1H,H_3,$J_{H_2H_3}$=11Hz & $J_{H_3H_4}$=11Hz), 5.92(d,1H,H_5,$J_{H_4H_5}$=3Hz), 6.70-7.33(m,9H,Ar-H)
4i	H		1600,1545,1305	2.43(s,6H,$N(CH_3)_2$), 4.20(dd, 1H,H_4,$J_{H_3H_4}$=11Hz & $J_{H_4H_5}$=3Hz), 4.90(d,1H,H_2,$J_{H_2H_3}$=11Hz),5.16 (dd,1H,H_3,$J_{H_2H_3}$=11Hz & $J_{H_3H_4}$= 11Hz), 5.92(d,1H,H_5,$J_{H_4H_5}$=3Hz), 6.17-6.56(m,2H, ), 7.2-7.8 (m,6H,Ar-H, ).

Table 2: Contd.....

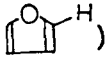
Compounds	R	R_1	IR(KBr) ν_{max} cm^{-1}	^1H NMR($CDCl_3$) δppm
5a	CH_3	C_6H_5	1625,1500,1300	2.36(s,3H,C_6H_4-CH_3), 5.69(s, 1H,H_2), 6.63(d,1H,H_5,J=7-8Hz), 7.13-7.50(m,9H,Ar-H),8.00(d, 1H,H_4,J=7-8Hz)
5b	CH_3	p-$OMeC_6H_4$	1600,1500,1300	2.42(s,3H,C_6H_4-CH_3), 3.76(s, 3H,OCH_3), 5.59(s,1H,H_2), 6.53 (d,1H,H_5,J=7-8Hz), 6.80-7.50 (m,8H,Ar-H), 7.83(d,1H,H_4, J=7-8Hz)
5c	CH_3		1625,1605,1500, 1300	2.25(s,3H,C_6H_4-CH_3), 5.70(s, 1H,H_2), 6.00-6.13(m,2H, ), 6.53(d,1H,H_5,J=7-8Hz), 7.00-7.43(m,5H,Ar-H and ), 7.78(d,1H,H_4,J=7-8Hz)
5d	Cl	C_6H_5	1630,1500,1300	5.66(s,1H,H_2), 6.59(d,1H,H_5, J=7-8Hz), 7.16-7.50(m,9H, Ar-H), 7.82(d,1H,H_4,J=7-8Hz)

Table 2: Contd....

Compounds	R	R_1	IR(KBr) ν_{max} cm^{-1}	^1H NMR($CDCl_3$) δ ppm
5e	Cl	p-$OMeC_6H_4$	1600,1500,1300	3.69(s,3H,OCH_3), 5.59(s,1H,H_2), 6.50(d,1H,H_5,J=7-8Hz), 6.70-7.50(m,8H,Ar-H), 7.85(d,1H,H_4,J=7-8Hz)
5f	Cl		1615,1510,1300	5.85(s,1H,H_2), 6.10-6.29(m,2H, ), 6.69(d,1H,H_5, J=7-8Hz), 7.06-7.52(m,5H,Ar-H & ), 7.82(d,1H,H_4,J=7-8Hz)
5g	C_6H_5	C_6H_5	1620,1500,1300	5.71(s,1H,H_2), 6.66(d,1H,H_5, J=7-8Hz), 7.22-7.96(m,10H, Ar-H), 8.04(d,1H,H_4,J=7-8Hz)
5h	C_6H_5	p-$OMeC_6H_4$	1610,1500,1315	3.73(s,3H,OCH_3), 5.59(s,1H,H_2), 6.50(d,1H,H_5,J=7-8Hz), 7.03-7.63(m,9H,Ar-H),7.90(d,1H,H_4, J=7-8Hz)

Table 2: Contd...

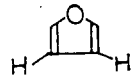
Compounds	R	R_1	IR(KBr) ν_{max} cm^{-1}	^1H NMR($CDCl_3$) δ ppm
5i	C_6H_5		1625,1500,1300	5.69(s,1H,H_2), 6.00-6.20(m, 2H, ), 6.59(d,1H, H_5,J=7-8Hz), 7.00-7.56(m,5H, Ar-H and ), 7.69(dm1H, H_4,J=7-8Hz)

Table 3: Physical and analytical data for compounds 7a-7e and 8a-8e

Compound	R	R_1	Yield %	m.p. °C	Calc. found	Analysis % C	H	N	Molecular formula	M/z
7a	CH_3	C_6H_5	75	116		71.64 72.08	5.47 5.59	6.96 7.06	$C_{24}H_{22}N_2O_2S$	149 (M^+-253) 253 (M^+-149)
7b	Cl	C_6H_5	78	132		65.32 65.92	4.49 4.21	6.63 6.39	$C_{23}H_{19}ClN_2O_2S$	149 (M^+-273) 273 (M^+-149)
7c	H	C_6H_5	74	147		71.13 71.64	5.15 5.20	7.21 7.00	$C_{23}H_{20}N_2O_2S$	149 (M^+-239) 239 (M^+-149)
7d	H	p-$OCH_3C_6H_4$	72	96		68.90 69.05	5.26 5.17	6.69 6.45	$C_{24}H_{22}N_2O_3S$	179 (M^+-239) 239 (M^+-179)
7e	p-Cl	p-$OCH_3C_6H_4$	70	77		63.64 64.03	4.64 4.35	6.19 6.38	$C_{24}H_{21}ClN_2O_3S$	179 (M^+-273) 273 (M^+-179)
8a	CH_3	C_6H_5	80	128		71.64 72.18	5.47 5.63	6.96 6.80	$C_{24}H_{22}N_2O_2S$	402 (M^+) 149 (M^+-253) 253 (M^+-149)
8b	Cl	C_6H_5	76	142		65.32 66.05	4.49 4.38	6.63 6.52	$C_{23}H_{19}ClN_2O_2S$	422 (M^+) 149 (M^+-273) 273 (M^+-149)

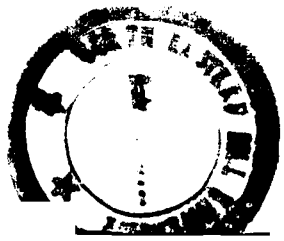


Table 3: Contd....

Compound	R	R_1	Yield %	m.p. °C	Calc. Found	Analysis % C	H	N	Molecular formula	M/z
8c	H	C_6H_5	74	167		71.13 71.64	5.15 5.20	7.21 7.00	$C_{23}H_{20}N_2O_2S$	388 (M^+) 149 (M^+-239) 239 (M^+-149)
8d	H	p-$OCH_3C_6H_4$	70	145		68.90 69.30	5.26 5.08	6.69 6.44	$C_{24}H_{22}N_2O_2S$	418 (M^+) 179 (M^+-239) 239 (M^+-179)
8e	Cl	p-$OCH_3C_6H_4$	71	164		63.64 64.08	4.64 4.18	6.19 6.07	$C_{24}H_{21}ClN_2O_3S$	452 (M^+) 179 (M^+-273) 273 (M^+-179)

Table 4: Spectral data for compounds 7a-7e and 8a-8e

Compound	R	R_1	IR(KBr) ν_{max} cm^{-1}	^1H NMR($CDCl_3$) δ ppm
7a	CH_3	C_6H_5	3400,1610,1545	2.20(s,3H,C_6H_4-CH_3), 3.76(bd,1H, NH), 4.80(dd,1H,H_4,$J_{H_3H_4}$=4Hz, $J_{H_4H_5}$=6Hz), 5.00(d,H_2,$J_{2,3}$=~11Hz), 5.36(dd,H_3,$J_{2,3}$=11Hz and $J_{3,4}$=4Hz), 6.18(d,H_5,$J_{4,5}$=6Hz), 6.50(d,2H,H_a), 6.96(d,2H,H_b,$J_{a,b}$=8Hz), 7.13-7.60 (m,10H,Ar-H)
7b	Cl	C_6H_5	3395,1595,1550	3.95(bd,1H,NH), 4.80(dd,H_4,$J_{3,4}$= 4Hz and $J_{H_4H_5}$=6Hz), 5.38(dd,H_3, $J_{H_2H_3}$=11Hz & $J_{H_3H_4}$=4Hz), 6.15(d, H_5,$J_{H_4H_5}$=6Hz), 6.52(d,2H,H_a), 7.10 (d,2H,H_b,$J_{a,b}$=8Hz), 7.26-7.65(m, 10H,Ar-H)
7c	H	C_6H_5	3390,1600,1545	3.93(bd,1H,NH), 4.86(dd,H_4,$J_{H_3H_4}$= 4Hz and $J_{H_4H_5}$=5Hz), 5.00(d,H_2, $J_{H_2H_3}$=11Hz), 5.40(dd,H_3,$J_{H_2H_3}$=11Hz and $J_{H_3H_4}$=4Hz), 6.20(d,H_5,$J_{H_4H_5}$=6Hz), 6.60(d,2H,H_a),6.82(d,2H,H_b,$J_{a,b}$=8Hz), 7.00-7.60(m,11H,Ar-H)

Table 4: Contd.....

Compound	R	R_1	IR(KBr) ν_{max} cm^{-1}	^1H NMR($CDCl_3$) δ ppm
7d	H	p-$OCH_3C_6H_4$	3395,1600,1550	3.76(s,3H,OCH_3), 3.90(bd,1H,NH), 4.82(dd,H_4,$J_{H_3H_4}$=4Hz & $J_{H_4H_5}$=6Hz), 4.93(d,H_2,$J_{H_2H_3}$=11Hz), 5.35(dd,H_3, $J_{H_2H_3}$=11Hz & $J_{H_3H_4}$=4Hz), 6.15(d, H_5,$J_{H_4H_5}$=6Hz), 6.56(d,2H,H_a), 6.78 (d,2H,H_b,$J_{H_aH_b}$=8Hz), 6.93-7.53(m, 10H,Ar-H)
7e	Cl	p-$OCH_3C_6H_4$	3400,1600,1550	3.73(s,3H,OCH_3), 3.90(bd,1H,NH), 4.73(dd,H_4,$J_{H_3H_4}$=4Hz & $J_{H_4H_5}$=6Hz), 4.90(d,1H,H_2,$J_{H_2H_3}$=11Hz), 5.23(dd, 1H,H_3,$J_{H_2H_3}$=11Hz & $J_{H_3H_4}$=4Hz), 6.08(d,1H,H_5,$J_{H_4H_5}$=6Hz), 6.46(d, 2H,H_a), 6.85(d,2H,H_b,$J_{a,b}$=8Hz), 7.05-7.60(m,9H,Ar-H)
8a	CH_3	C_6H_5	3400,1610,1550	2.23(s,3H,CH_3), 3.63(bd,1H,NH),4.95 (d,H_2,$J_{H_2H_3}$=11Hz), 5.09(dd,H_4,$J_{H_3H_4}$= 11Hz & $J_{H_4H_5}$=3Hz), 5.31(dd,H_3,

Table 4: Contd...

Compound	R	R_1	IR(KBr) ν_{max} cm^{-1}	^1H NMR($CDCl_3$) δ ppm
				$J_{H_2H_3}=J_{H_3H_4}$=11Hz), 6.03(d,1H,H_5, $J_{H_4H_5}$=3Hz), 6.63(d,2H,H_a), 7.02 (d,2H,H_b,$J_{a,b}$=8Hz), 7.13-7.53(m, 10H,Ar-H)
* 8b	Cl	C_6H_5	3400,1610,1550	3.73(bd,1H,NH), 4.95(d,1H,H_2, $J_{H_2H_3}$=11Hz), 5.05(dd,1H,H_4,$J_{H_3H_4}$= 11Hz and $J_{H_4H_5}$=3Hz), 5.43(dd,1H, H_3,$J_{H_2H_3}=J_{H_3H_4}$=11Hz), 5.98(d,1H, H_5,$J_{H_4H_5}$=3Hz), 6.65(d,2H,H_a), 7.13 (d,2H,H_b,$J_{a,b}$=8Hz), 7.25-7.65(m, 10H,Ar-H)
8c	H	C_6H_5	3340,1600,1550	3.73(bd,1H,NH),4.98(d,1H,H_2,$J_{H_2H_3}$= 11Hz), 5.08(dd,1H,H_4,$J_{H_3H_4}$=11Hz & $J_{H_4H_5}$=3Hz), 5.34(dd,1H,H_3,$J_{H_2H_3}$= 11Hz), 6.03(d,1H,H_5,$J_{H_4H_5}$=3Hz), 6.72(m,3H,H_a and H_c), 6.83(d,2H, H_b,$J_{a,b}$=8Hz), 7.1-7.53(m,10H,Ar-H)

* in $CDCl_3/D_3CCOCD_3$

Table 4: Contd.....

Compounds	R	R_1	IR(KBr) ν_{max} cm^{-1}	^1H NMR($CDCl_3$) δ ppm
8d	H	p-$OCH_3C_6H_4$	3400,1600,1550	3.76(s,3H,OCH_3), 3.80(bd,1H,NH), 4.92(d,1H,H_2,$J_{H_2H_3}$=11Hz), 5.06 (dd,1H,H_4,$J_{H_3H_4}$=11Hz & $J_{H_4H_5$=3Hz), 5.30(dd,1H,H_3,$J_{H_2H_3}$= $J_{H_3H_4}$=11Hz), 6.00(d,1H,H_5,$J_{H_4H_5}$=3Hz), 6.70(d, 2H,H_a), 6.86(d,2H,H_b,$J_{a,b}$= 8Hz), 7.00-7.50(m,10H,Ar-H)
8e	Cl	p-$OCH_3C_6H_4$	3400,1600,1550	3.77(s,3H,OCH_3), 3.93(bd,1H,NH), 4.93(d,1H,H_2,$J_{H_2H_3}$=11Hz), 5.10(dd, 1H,H_4,$J_{H_3H_4}$=11Hz,$J_{H_4H_5}$=3Hz), 5.35 (dd,1H,H_3,$J_{H_2H_3}$=$J_{H_3H_4}$=11Hz), 5.96 (d,1H,H_5,$J_{H_4H_5}$=3Hz), 6.63(d,2H,H_a), 6.87(d,2H,H_b,$J_{a,b}$=8Hz), 7.00-7.66 (m,10H,Ar-H)

Table 5: Physical and analytical data for compounds 11a-11j

Compound	R	R_1	m.p. °C	Yield %	Mol. formula	MS	Calc. / Found	Analysis % C	H	N
11a	CH_3	H	141	66	$C_{18}H_{17}NO_2S$	311 (M^+)	Calc.	69.45	5.47	4.50
							Found	69.61	5.32	4.38
11b	CH_3	CH_3	124	63	$C_{19}H_{19}NO_2S$	325 (M^+)	Calc.	70.15	5.85	4.31
							Found	70.43	5.92	4.37
11c	CH_3	Br	151	51	$C_{18}H_{16}BrNO_2S$	390 (M^+)	Calc.	55.38	4.10	3.59
							Found	55.61	3.85	3.59
11d	Cl	H	152	57	$C_{17}H_{14}ClNO_2S$	331 (M^+)	Calc.	61.54	4.22	4.22
							Found	61.79	4.27	4.01
11e	Cl	CH_3	126	72	$C_{18}H_{16}ClNO_2S$	345 (M^+)	Calc.	62.51	4.63	4.05
							Found	62.55	4.70	4.01
11f	Cl	Br	140	50	$C_{17}H_{13}BrClNO_2S$	410 (M^+)	Calc.	49.69	3.17	3.41
							Found	50.08	3.05	3.41
11g	Br	H	134	65	$C_{17}H_{14}BrNO_2S$	376 (M^+)	Calc.	54.25	3.72	3.72
							Found	54.42	3.68	3.73
11h	H	H	120	57	$C_{17}H_{15}NO_2S$	297 (M^+)	Calc.	68.68	5.05	4.71
							Found	69.01	5.01	4.64
11i	H	CH_3	138	59	$C_{18}H_{17}NO_2S$	311 (M^+)	Calc.	69.45	5.47	4.50
							Found	69.32	5.36	4.64
11j	H	Br	132	64	$C_{17}H_{14}BrNO_2S$	376 (M^+)	Calc.	54.25	3.72	3.72
							Found	54.63	3.75	3.76

Table 6: Spectral data for compounds 11a-11j

Compounds	R	R_1	IR(KBr) ν_{max} cm^{-1}	^{1}H NMR($CDCl_3$) δppm
11a	CH_3	H	3200,1620,1540	2.33(s,3H,CH_3), 4.15(s,2H,-CH_2-), 6.27(d,1H,=C-H,J=8Hz), 7.06-7.51 (m,9H,Ar-H), 9.24(d,1H,-C(=O)-H), 9.45 (b,1H,N-OH)
11b	CH_3	CH_3	3371,1647,1564	2.33(s,6H,2CH_3), 4.12(s,2H,-CH_2-), 6.27(d,1H,=C-H,J=8Hz), 7.09-7.45 (m,8H,Ar-H), 9.21(d,1H,-C(=O)-H), 9.40 (b,1H,N-OH)
11c	CH_3	Br	3360,1640,1540	2.36(s,3H,CH_3), 4.12(s,2H,-CH_2-), 6.33(d,1H,=C-H , J=8Hz), 7.21-7.42 (m,8H,Ar-H), 9.24(d,1H,-C(=O)-H), 9.54 (b,1H,N-OH)
11d	Cl	H	3200,1630,1540	4.36(s,2H,-CH_2-), 6.45(d,1H,=C-H, J=8Hz), 7.24-7.57(m,9H,Ar-H), 9.06 (d,1H,-C(=O)-H), 9.29(b,1H,N-OH)
11e	Cl	CH_3	3162,1629,1563	2.33(s,3H,CH_3), 4.15(s,2H,-CH_2-), 6.33(d,1H,=C-H,J=8Hz), 7.12-7.45(m, 8H,Ar-H), 9.22(d,1H,-C(=O)-H),9.9(b,1H, N-OH)

Table 6: Contd...

Compounds	R	R_1	IR(KBr) ν_{max} cm^{-1}	^1H NMR($CDCl_3$) δ ppm
11f	Cl	Br	3370,1645,1550	4.15(s,2H,$-CH_2-$), 6.34(d,1H,=C-H, J=8Hz), 7.18-7.42(m,8H,Ar-H), 9.18 (d,1H,$-\overset{\overset{O}{\|}}{C}-H$), 9.85(b,1H,N-OH)
11g	Br	H	3160,1625,1565	4.18(s,2H,$-CH_2-$), 6.33(d,1H,=C-H, J=8Hz), 7.15-7.66(m,9H,Ar-H), 9.18 (d,1H,$-\overset{\overset{O}{\|}}{C}-H$), 9.60(b,1H,N-OH)
11h	H	H	3200,1630,1540	4.17(s,2H,$-CH_2-$), 6.30(d,1H,=C-H , J=8Hz), 7.30-7.60(m,10H,Ar-H), 9.24 (d,1H,$-\overset{\overset{O}{\|}}{C}-H$), 10.00(b,1H,N-OH)
11i	H	CH_3	3250,1640,1540	2.33(s,3H,CH_3), 4.12(s,2H,$-CH_2-$), 6.30(d,1H,=C-H , J=8Hz), 7.10-7.48 (m,9H,Ar-H), 9.21(d,1H,$-\overset{\overset{O}{\|}}{C}-H$), 9.50 (b,1H,N-OH)
11j	H	Br	3190,1629,1551	4.12(s,2H,$-CH_2-$), 6.30(d,1H,=C-H , J=8Hz), 7.18-7.42(m,9H,Ar-H), 9.18 (d,1H,$-\overset{\overset{O}{\|}}{C}-H$), 9.42(b,1H,N-OH)

Table 7: Physical and analytical data for compounds 19a-19c and 21a-21d

Compounds	R	m.p. °C	Yield %	Mol. formula	Calc. / Found	Analysis % C	H	N	M/z
19a	H	75	87	$C_{18}H_{23}NS$ (285)		75.79	8.07	4.91	285(M^+)
						75.61	8.17	4.96	191(M^+-94)
19b	p-CH_3	104	89	$C_{19}H_{25}NS$ (299)		76.25	8.36	4.68	299(M^+)
						76.42	8.25	4.59	205(M^+-94)
19c	p-Cl	110	92	$C_{18}H_{22}ClNS$ (319.5)		67.60	6.88	4.38	319(M^+)
						67.78	7.06	4.41	225(M^+-94)
21a	H	71	65	$C_{21}H_{25}NS$ (323)		78.02	7.74	4.33	323(M^+)
						78.61	7.50	4.08	191(M^+-132)
21b	p-CH_3	116	67	$C_{22}H_{27}NS$ (337)		78.34	8.01	4.15	337(M^+)
						78.85	7.68	4.09	205(M^+-132)
21c	p-Cl	135	68	$C_{21}H_{24}ClNS$ (357.5)		70.49	6.71	3.92	357(M^+)
						71.09	6.58	3.73	225(M^+-132)
21d	p-Br	145	63	$C_{21}H_{24}BrNS$ (402)		62.69	5.97	3.48	402(M^+)
						63.05	5.72	3.39	270(M^+-132)

Table 8: Spectral data for compounds 19a-19c and 21a-21d

Compound	R	IR(KBr) ν_{max} cm^{-1}	^{13}C NMR($CDCl_3$) δppm	^{1}H NMR($CDCl_3$) δppm
19a	H	1590,1475,1445	29.13(C-9),29.93(C-10), 34.41(C-11), 41.04(C-1/C-8), 41.92($N(CH_3)_2$, 43.39(C-8/C-1),51.17 (C-7), 52.87(C-2),66.60 (C-6),123.63(C-5),139.38 (C-4), 123.64,126.17, 128.36,128.77(Ar)	1.10-2.60(m,9H),2.36(s,6H, $N(CH_3)_2$), 3.02(dd,1H,H_6, $J_{6,7}$=8Hz & $J_{5,6}$=4Hz), 3.06 (dd,1H,H_2,$J_{1,2}$=2Hz & $J_{2,7}$= 8Hz), 6.58(d,1H,H_5,$J_{5,6}$= 4Hz), 7.23-7.67(m,5H,Ar-H)
19b	CH_3	1585,1480,1445		1.10-2.23(m,8H),2.30(s,3H, CH_3), 2.40(s,6H,$N(CH_3)_2$), 2.60-3.10(m,3H), 6.56(d,1H, H_5,$J_{H_5H_6}$=4Hz), 7.03-7.50(m, 4H,Ar-H)
19c	Cl	1585,1480,1450	29.06(C-9),29.84(C-10), 34.34(C-11), 40.96(C-1/C-8),41.87($N(CH_3)_2$), 43.28(C-8/C-1), 51.15	1.10-2.26(m,8H),2.40(s,6H, $N(CH_3)_2$), 2.42-2.65(m,1H), 3.04(dd,1H,H_6,$J_{H_6H_7}$=8Hz, $J_{H_5H_6}$=4Hz), 3.10(dd,1H,H_2,

Table 8: Contd..

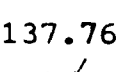
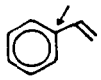
Compound	R	IR(KBr) ν_{max} cm^{-1}	^{13}C NMR($CDCl_3$) δppm	^{1}H NMR($CDCl_3$) δppm
			(C-7), 52.84(C-2), 66.62 (C-6), 124.16(C-5), 138.24 (C-4), 137.76(Cl- ), 133.65(), 127.37, 127.77, 128.41(Ar)	$J_{H_2H_7}$=8Hz, $J_{H_1H_2}$=2Hz), 6.56 (d,1H,H_5, $J_{H_5H_6}$=4Hz), 7.23-7.56(m,4H,Ar-H)
21a	H	1600,1590,1490, 1440		1.48-1.90(m,2H), 2.12-2.34 (m,3H), 2.38(s,6H,$N(CH_3)_2$), 2.50-2.70(m,3H), 3.00-3.24 (m,3H), 5.50-5.68(m,2H,H_{11} and H_{12}), 6.51(d,1H,H_5, $J_{H_5H_6}$= 4Hz), 7.17-7.57(m,5H,Ar-H)
21b	CH_3	1600,1595,1500, 1440		1.45-2.34(m,5H), 2.34(s,3H, CH_3-Ph), 2.40(s,6H,$N(CH_3)_2$), 2.50-3.21(m,6H), 5.60(m,2H, H_{11} and H_{12}), 6.50(d,1H,H_5, $J_{H_5H_6}$=4Hz), 7.10-7.50(m,4H, Ar-H)

Table 8: Contd...

Compound	R	IR(KBr) ν_{max} cm^{-1}	^{13}CNMR($CDCl_3$) δppm	^{1}H NMR($CDCl_3$) δppm
21c	Cl	1600,1590,1490, 1440		1.45-1.90(m,2H), 2.10-2.33(m, 3H), 2.38(s,6H,$N(CH_3)_2$), 2.51-2.72(m,3H), 3.00-3.24 (m,3H), 5.50-5.70(m,2H),H_{11} and H_{12}), 6.50(d,1H,H_5, $H_{H_5H_6}$=4Hz), 7.15-7.50(bd,4H, J=8Hz)
21d	Br	1600,1590,1490, 1440		1.46-2.26(m,5H), 2.36(s,6H, $N(CH_3)_2$), 2.45-3.26(m,6H), 5.60(m,2H,H_{11} and H_{12}), 6.50(d,1H,H_5,$J_{H_5H_6}$=4Hz), 7.20-7.50(bd,4H,J=8Hz)

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CHAPTER IV

REACTIONS OF THIOAMIDE VINYLOGS WITH ISONITRILES AND ISOTHIOCYANATES

AND

REACTIONS OF N,N-DIMETHYL-N'-THIOBENZOYLFORMAMIDINE AND N,N-DIMETHYL-N'-PHENYLTHIOCARBAMOYLFORMAMIDINE WITH IMIDOYL CHLORIDES

4.1 Reactions of thioamide vinylogs with isonitriles and isothiocyanates:

4.1.1 INTRODUCTION:

As discussed in earlier chapters the thioamide vinylogs have been known to undergo a variety of nucleophilic[1-4],

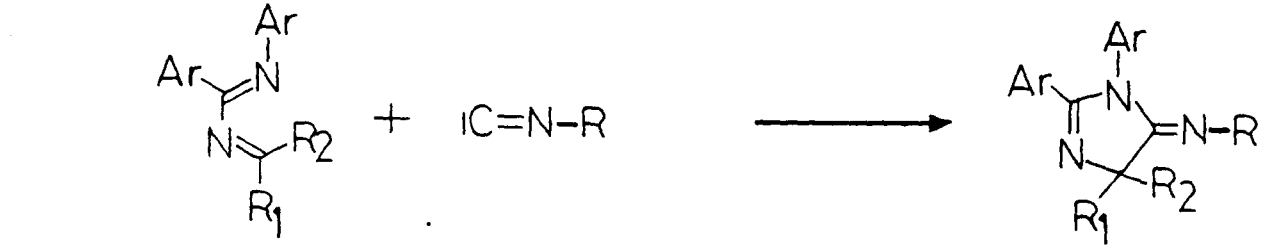
electrophilic[5-7] and cycloaddition reactions[8-12] resulting in numerous heterocyclic compounds. But there is no report in literature concerning the reactions of thioamide vinylogs with substrates having a carbon nitrogen double or tripple bond. The isonitriles which display the carbene characteristics have been known to react with some heterodienes in a (1+4) cycloaddition manner[13,14]. Also the isothiocyanates have been known to undergo cycloaddition reactions with various heterodienes[15]. Keeping all these in mind we considered it worthwhile to investigate the reactions of thioamide vinylogs with isonitriles and isothiocyanates. The results of these investigations are presented below.

RESULTS AND DISCUSSIONS:

4.1.2 Reactions of thioamide vinylogs derived from secondary amines with isonitriles:

The treatment of thioamide vinylogs (1a) derived from secondary amines with an equivalent amount of alkyl/aryl-isonitriles (2) in refluxing dry dioxane resulted unexpectedly in thioamide vinylogs derived from primary amines (3)[16]. The products have been characterised as 3-aryl-amino/cyclohexylamino-1-arylpropene-1-thiones (3) on the basis of analytical and spectral data (Tables 1 and 2). The ^{1}H NMR spectra of compounds 3 in general, displayed two doublets of one proton each at δ 6.50-6.65 and δ 7.60-7.75 assignable to vinylic protons H_a and H_b

respectively. This is expected as the vinylic proton H_b is less shielded because of the deshielding effect of nitrogen attached to carbon bearing this proton. Also, the vinylic proton H_a is expected to appear at lower δ value because of the resonance effect of nonbonding electron pair at nitrogen. The aromatic protons appeared as a multiplet in the region δ7.10-7.90 and a low field broad peak~δ 13.50-15.40 which is exchangeable with D_2O is assigned to the NH proton. In the case of compounds 3e-3g the methylene protons appeared as a doublet around δ 4.50(J=6Hz) probably because of splitting of these protons by the NH proton attached to it. In case of products 3h-3k the methine proton appeared as unresolved multiplet around δ 3.25 and methylene protons as multiplet in the region δ 1.30-2.10. These products have been assigned z-configuration on the basis of the coupling constant of two vinylic protons ($J_{a,b}$=7-8Hz). The preferred z-configuration in these cases could be due to the intramolecular hydrogen bonding[17]. Further confirmation for the structure 3 is derived from their mass spectra and by comparison of their melting points with that of the authentic samples. A number of futile attempts were made to isolate the cycloadducts of the type shown in Scheme 1 and resulted invariably in the thiones 3 as the only isolable products. For example, the treatment of an equimolar mixture of 1 and 2 in dioxane with $BF_3.Et_2O$ resulted in spontaneous conversion of 1 to 3.



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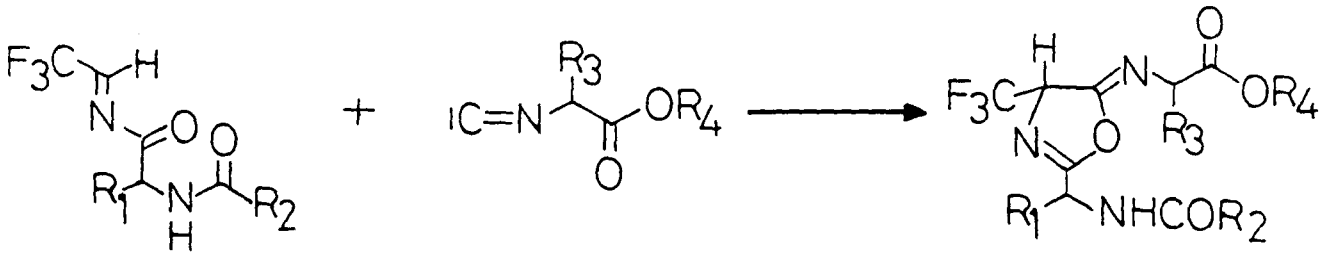


Ref 14

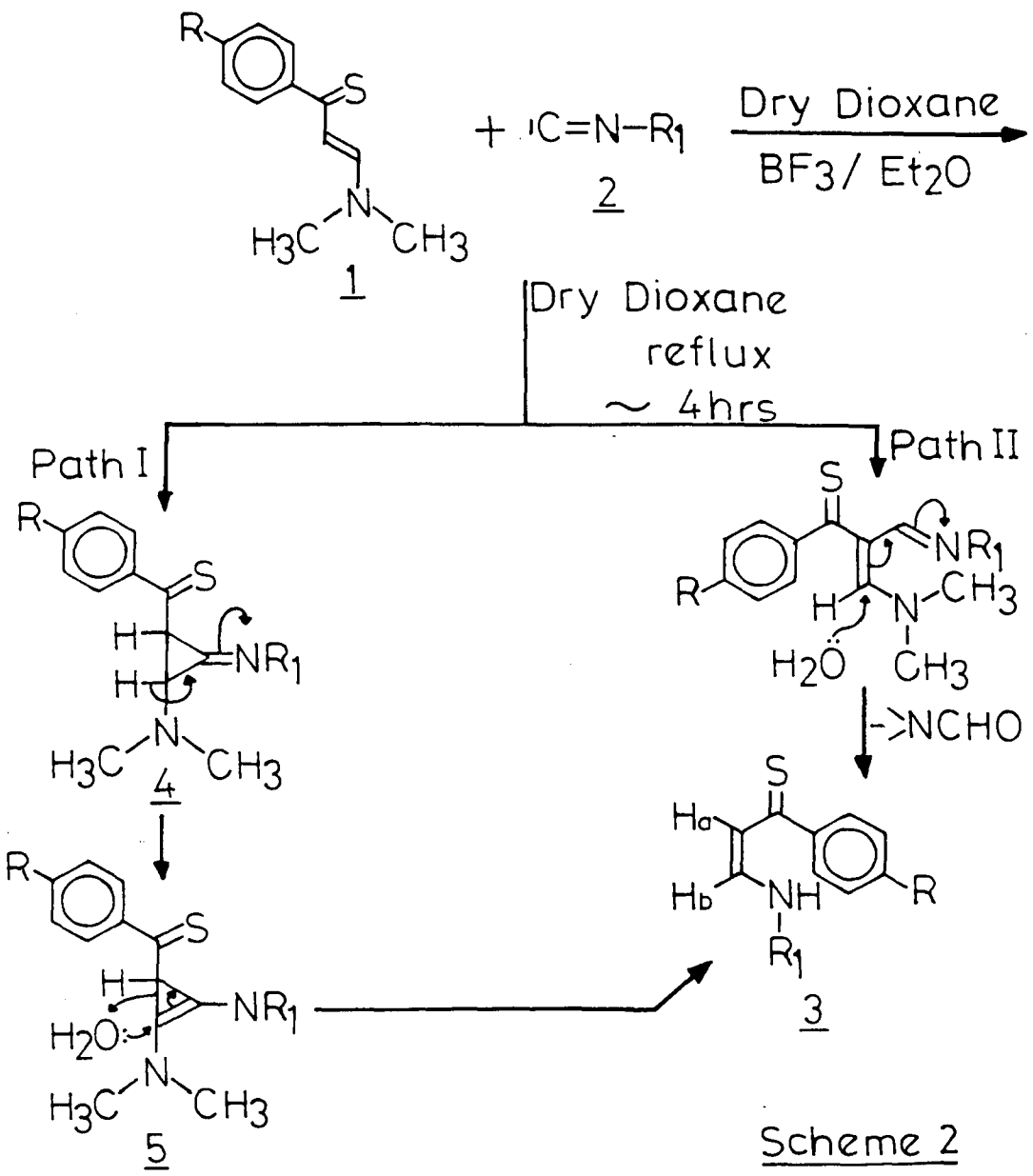
Scheme 1

The reaction of 1 and 2 in refluxing dry benzene required much longer reaction periods for conversion to 3.

The mechanistic pathways leading to the formation of 3 are outlined in the scheme 2. Of these, the pathway I is less likely because it involves the formation of highly strained iminocyclopropane intermediate 4 via (1+2) cycloaddition reactions of thioamide vinylogs with isonitriles. The intermediate 4 is presumed to isomerise to intermediate 5 which in turn undergoes hydrolytic cleavage to afford 3. The pathway II is more likely and is presumed to involve the initial electrophilic attack of isonitriles at C-2 of the thioamide vinylogs. This is interesting and intriguing case of electrophilic attack at C-2 of thioamide vinylogs since in all reported reactions the electrophilic attack is known to take place exclusively at sulphur[17]. This aspects of the chemistry of thioamide vinylogs needs careful and systematic further exploration.

4.1.3 Reactions of thioamide vinylogs (3-morpholino-1-phenylpropene-1-thione) with N-arylisothiocyanates:

The reactions of an equimolar mixture of 3-morpholino-1-phenylpropene-1-thione (7) and N-arylisothiocyanates in refluxing dry acetonitrile resulted unexpectedly in N-(N-arylthiocarbamoyl) morpholine (8) as the only isolable products. The identities of 8 were established on the basis of analytical and spectral data (Tables 3 and 4).



1 2 3 4 5

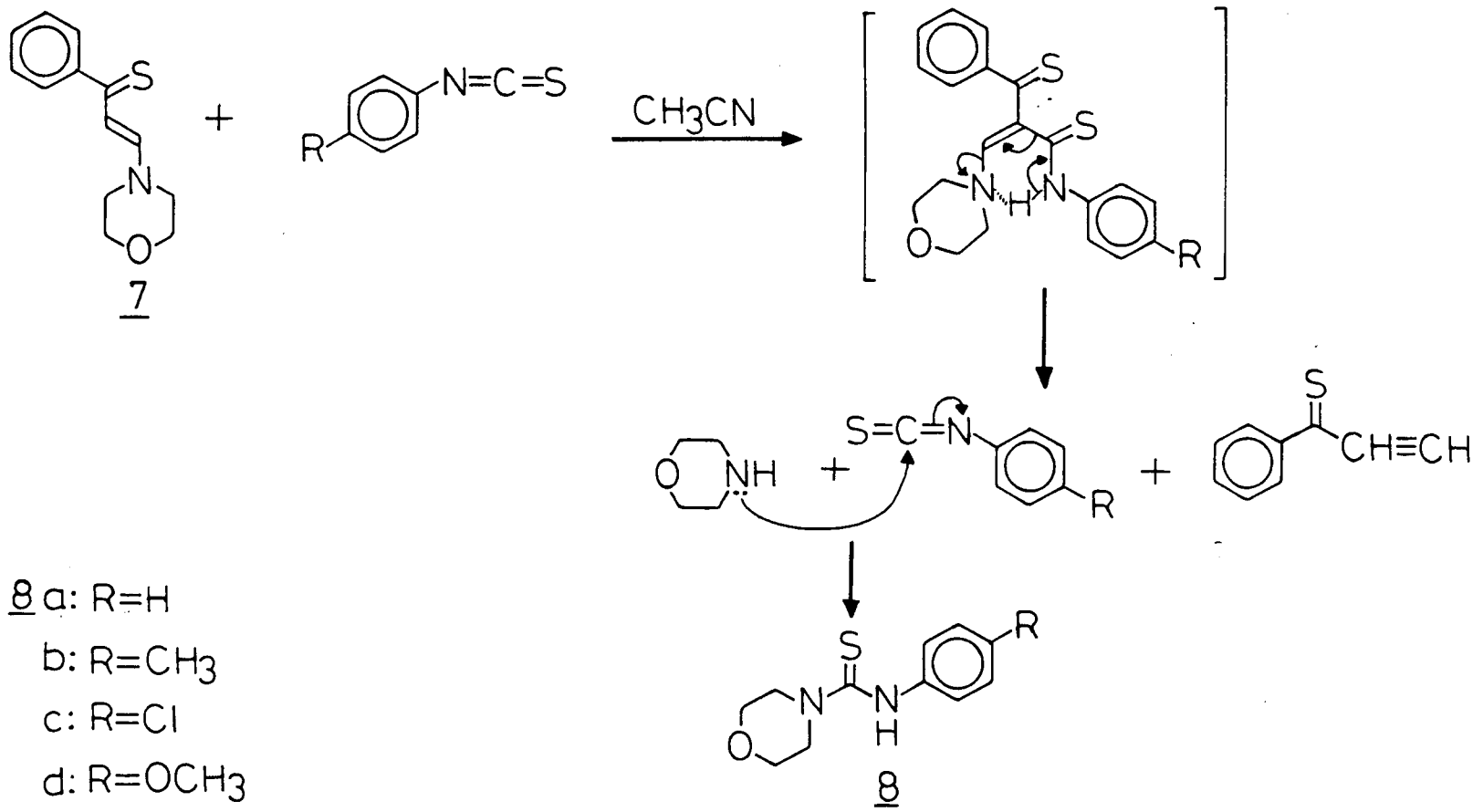
Scheme 2

3a: R=H, R_1=C_6H_5
b: R=CH_3, R_1=C_6H_5
c: R=Cl , R_1=C_6H_5
d: R=Br , R_1=C_6H_5
e: R=H , R_1=H_2C-C_6H_5
f: R=Cl , R_1=H_2C-C_6H_5
g: R=Br , R_1=H_2C-C_6H_5
h: R=H , R_1=Cyclohexyl
i: R=CH_3, R_1=Cyclohexyl
j: R=Cl , R_1=Cyclohexyl
k: R=Br , R_1=Cyclohexyl

The ^1H NMR spectra of 8 exhibited a singlet for eight protons ~δ 3.70-3.80 assignable to eight morpholine protons. The aromatic protons appeared as a multiplet in the region δ 6.80-7.40 and a broad peak ~δ7.40 which is exchangeable with D_2O was assigned to the NH proton. Further confirmation to the structure of 8 was derived through its comparison with the authentic sample prepared by the reactions of morpholine with various N-arylisothiocyanates. The rationalisation for the formation of N-(N-arylthiocarbomoyl) morpholine 8 in these reactions is outlined in the Scheme 3. In this scheme it is presumed that the initial electrophilic attack of the carbon of isothiocyanates at the C-2 of the thioamide vinylogs results in an intermediate 2 which decomposes to arylisothiocyanates, morpholine and thiobenzoyl acetylene. The reaction of morpholine and N-arylisothiocyanates so formed results in the formation of 8. As already pointed out this is another case of unusual behaviour of thioamide vinylogs involving electrophilic attack at C-2 position. It is worthwhile to mention here that the thioamide vinylogs did not yield the cycloadducts with C=N of isothiocyanates and carbodiimides even under drastic reaction conditions.

4.2.1 Reactions of N,N-dimethyl-N′-thiobenzoylformamidine and N,N-dimethyl-N′-arylthiocarbamoylformamidines with N-arylbenzimidoyl chlorides[18]:

N,N-Dimethyl-N′-thiobenzoylformamidines (9) are known to



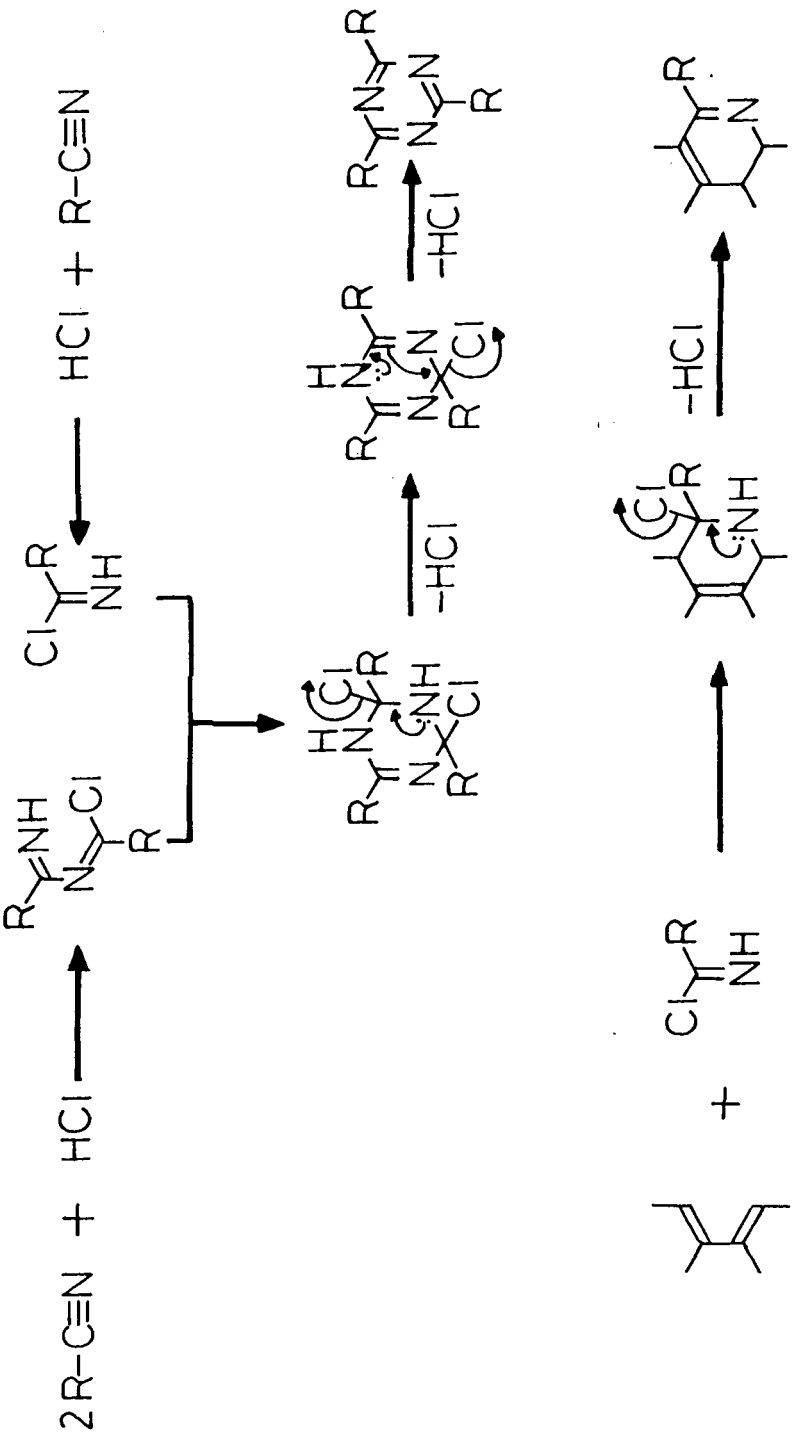
8 a: R=H
b: R=CH_3
c: R=Cl
d: R=OCH_3
e: R=OC_2H_5

Scheme 3

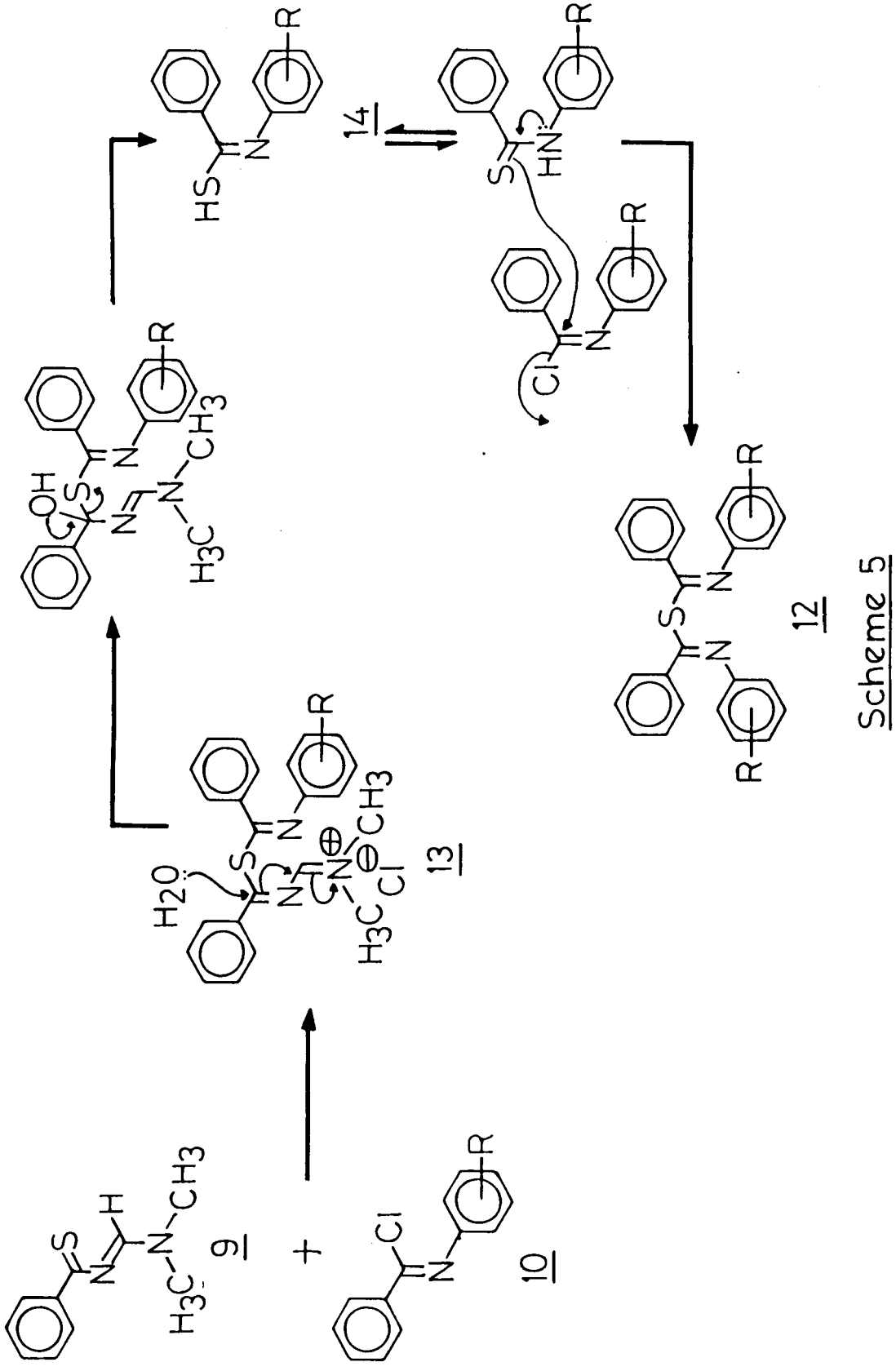
participate as 4 π component in (4+2) cycloaddition reactions with substrates like ketenes[19], sulfenes[20], α,ß-unsaturated substrates[21,22] etc. leading to the formation of a variety of heterocyclic compounds. Also, the electrophilic reactions occuring at sulphur atom of 9 are reported[19,20]. The literature survey revealed that the azadienes and all carbon dienes undergo (4+2) cycloadditions with substrates having carbon nitrogen double bond[23,15]. It has also been reported that imidoyl chloride adds to all carbon dienes in a (4+2) cycloaddition manner[23] (Scheme 4). But there have been no report in literature on the reactions of 9 with substrates having carbon nitrogen double bond. We have explored here the reactions of N,N-dimethyl-N'-thiobenzoylformamidine and N,N-dimethyl-N'-phenylthiocarbamoylformamidine (11) with various N-arylbenzimidoyl chlorides (10) in order to investigate the reaction pathways followed and the nature of the products formed in these cases.

4.2.2 RESULTS AND DISCUSSIONS:

The reactions of N,N-dimethyl-N'-thiobenzoylformamidines (9) with N-arylbenzimidoyl chlorides (10) in dry chloroform afforded very good yields (76-82%) of products which were characterised as dimidoyl sulfides (12) on the basis of analytical, spectral (ir, ^{1}H NMR and mass) data (Tables 5 and 6) and by melting point comparison with that of authentic sample. The probable mechanism leading to the formation of 12 is shown in Scheme 5. In this scheme it

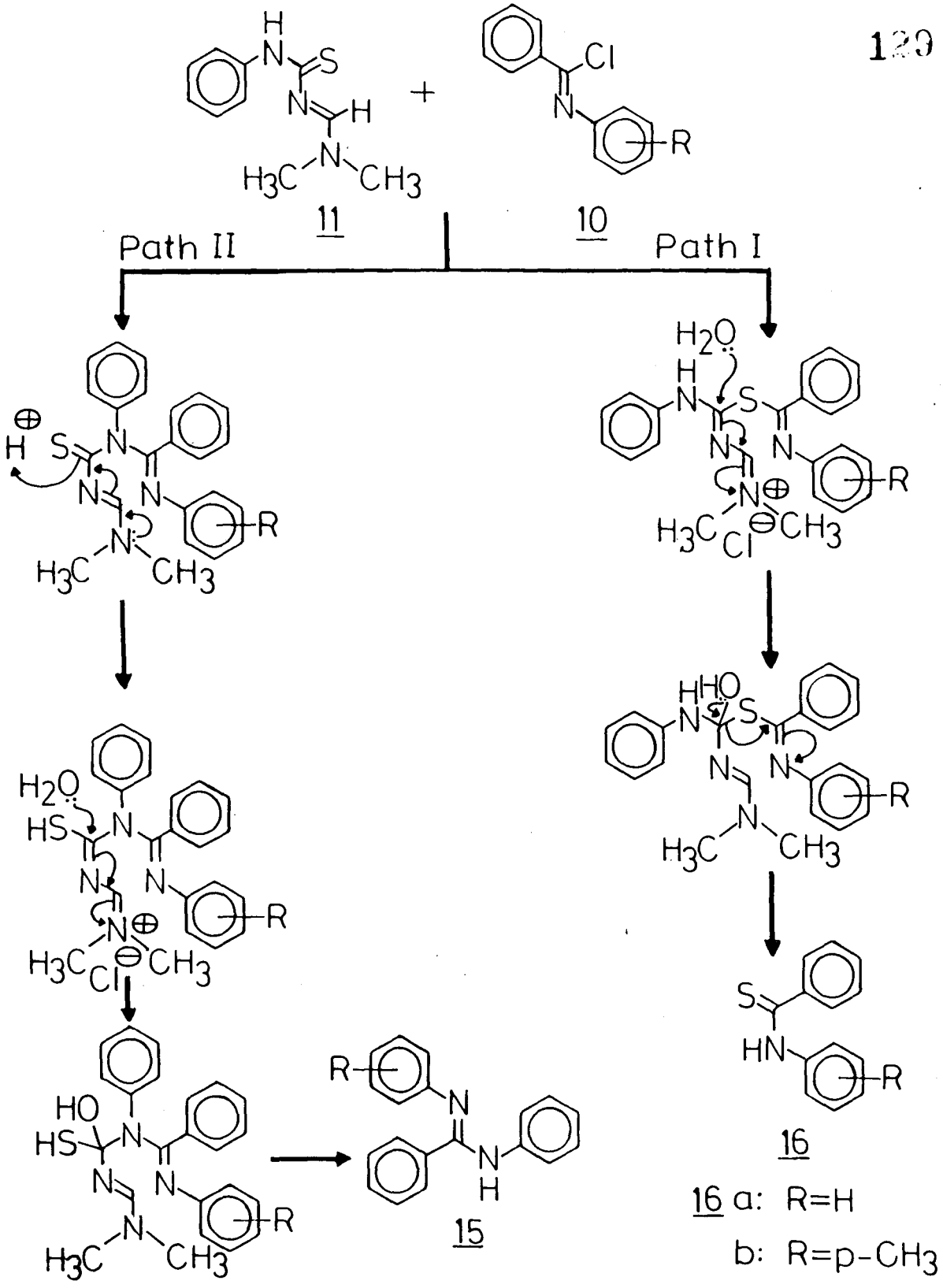


Scheme 4



Scheme 5

is presumed that 9 initially undergoes nucleophilic attack of sulphur at the imidoyl chlorides to give immonium salt (13) as the intermediate. The hydrolytic decomposition of this intermediate results in the formation of thiobenzanilide (14) which reacts with another molecule of 10 to yield the products 12. Further to our studies we have examined the reactions of N,N-dimethyl-N′-phenylthiocarbamoylformamidine (11), where the non-bonding electron pair at nitrogen attached to phenyl can also polarise the thiocarbonyl group, with benzimidoyl chlorides (10). Thus the reactions of equimolar amounts of 10a and 11, for example in refluxing dry THF gave a mixture of products consisting of N,N′-diphenylbenzamidine (15a:33%) and thiobenzanilide (16a;65%). A similar reaction of 11 with N-p-tolyl benzimidoyl chloride leads to the formation of N-p-tolyl-N′-phenylbenzamidine (15b; 30%) and N-p-tolylthiobenzanilide (16b; 68%). The reaction of 11 with other imidoyl chlorides (10e,f) resulted in thiobenzanilides (16c,d) as the only isolable products. The formation of 15 and 16 in these reactions could be rationalised in terms of mechanistic pathways indicated in Scheme 6. As shown in this scheme the reactions of 11 with 10 perhaps follow two different pathways. The reaction pathway I involving nucleophilic attack of sulphur leads to the formation of thiobenzanilides (16) whereas the reaction pathway II involving nucleophilic attack of nitrogen on


11
10
Path II
Path I
16
15
15 a: R=H
b: R=p-CH3
16 a: R=H
b: R=p-CH3
c: R=p-Cl
d: R=p-Br

Scheme 6

imidoyl chlorides results in the formation of N-aryl-N'-phenylbenzamidines (15). The structure of these products were elucidated on the basis of analytical and spectral data (Tables 7 and 8) and were found to be in conformity with the assigned structures. Further confirmation was derived through the comparison of their spectral data and melting points with those of reported ones. A number of futile attempts were made to carry out the desired cycloaddition reactions and even under extremely anhydrous reaction conditions resulted in the same products. The similar reactions of thioamide vinylogs with imidoyl chlorides resulted in an intractable mixtures from which no identifiable product could be isolated. Also, carbodiimides failed to react with 9 and 11 even under vigorous reaction conditions.

CONCLUSION:

The reactions studied here represent first few cases where thioamide vinylogs behave as enamines. The electrophilic attack at C-2 of the thioamide vinylogs is intriguing and needs further careful and systematic investigations. We have recently observed that the reactions of 3-arylamino-1-phenylpropene-1-thiones with N,N-dimethylformamide dimethylacetal resulted in 3-dimethylamino-1-phenylpropene-1-thione. This could also be rationalised by the initial electrophilic attack at C-2 of 3-arylamino-1-phenylpropene-1-thiones. The reactions of N,N-

dimethyl-N'-(arylthiocarbamoyl) formamidines with benzimidoyl chlorides led to thiobenzanilides, dimidoyl sulfides and amidines and their formation is mechanistically interesting.

4.3 EXPERIMENTAL SECTION:

General conditions were same as described in chapter II.

Starting Materials:

The commercial samples of acetophenone, 4-chloroacetophenone, 4-bromoacetophenone, 4-methylacetophenone, dioxane, acetonitrile, aniline, benzylamine, cyclohexylamine, p-toluidine, p-chloroaniline, p-anisidine, p-phenetidine, morpholine, N,N-dimethyl formamide and dimethyl sulphate were purified before use.

N,N-dimethylformamide dimethylacetal, b.p. 102°C[24]; 3-dimethylamino-1-phenyl propene-1-thione, m.p. 115-6°C[25]; 3-dimethylamino-1-p-chlorophenylpropene-1-thione, m.p. 119-20°C[25]; 3-dimethylamino-1-p-bromophenylpropene-1-thione, m.p. 118-19°C[25]; 3-dimethylamino-1-p-methylphenylpropene-1-thione, m.p. 135-36°C[25] were prepared by the reported methods.

Phenylisothiocyanate[26]; p-methylphenylisothiocyanate[26]; p-chlorophenylisothiocyanate[26]; p-methoxyphenylisothiocyanate[26] and p-ethoxyphenylisothiocyanate[26] were also prepared according to the reported procedures.

Preparation of isonitriles[27]:

A five hundred round-bottomed flask equipped with a magnetic stirrer and reflux condenser was charged with aniline (0.2 mol, 18.6g), alcohol free chloroform (0.2 mol, 2.4g), benzyltrimethylammonium chloride (0.5g) and dichloromethane

(60ml) and 50% aquous sodium hydroxide solution (60 ml) was added to it in one portion. After induction period of about ten minutes, the chloroform refluxes spontaneously and the reaction mixture was kept at a temperature of ca 40°C. After about one hour the refluxing ceases and the reaction mixture was further stirred for one more hour. The reaction mixture was then diluted with water (200 ml) and extracted with dichloromethane. The dichloromethane extract was washed with water, brine and dried over anhydrous magnesium sulfate. Distillation afforded the pure phenyl isonitrile, b.p. 50-52°C/11 torr.

The benzyl and cyclohexyl isonitriles were prepared similarly.

Preparation of 5-phenyl-1,2-dithiole-3-one[28]:

Three hundred ml (315g, 1.8 moles) of ethyl cinnamate was heated to boil in a 2 liter wide-mouth conical flask and 90g (2.8g atoms) of sulfur added to it. The sulfur dissolved readily and the mixture then was boiled gently for one hour cooled, diluted with 125 ml of ethanol,chilled thoroughly and filtered. The yield of fan product, m.p. 104-109° (lit.[28] m.p. 102-112°), was 165g(61%). It was recrystallised from ethanol, m.p. 113-115° (lit.[28] m.p. 114-117°).

Preparation of 5-phenyl-1,2-dithiole-3-thione[28]:

A solution of 20.0g (0.103 mol) of 5-phenyl-1,2-dithiole-3-one and 30.0g (0.135 mol) of phosphorous pentasulfide

in 200 ml of pyridine was refluxed for 4 hours. The reaction mixture was then cooled partially diluted with 150 ml of water, chilled and filtered. The yield of brown product, m.p. 114-117° (lit.[28] m.p. 116-119°), was 19g(88%). crystallisation from 150 ml of butyl acetate gave 16g of brown needles, m.p. 123-125°(lit.[28] m.p. 125-127°).

Preparation of 3-phenyl-1,2-dithioleum hydrogen sulfate[28]: Twelve grams (0.057 mol) of 5-phenyl-1,2-dithiole-3-thione was dissolved in 400 ml of acetone with gentle warming. The solution then was stirred in an ice bath and 32g(0.17 mol) of 40% peracetic acid was added during 15 minutes. In order to prevent crystallisation of starting material, the addition of peracetic acid was begun before the acetone solution was thoroughly chilled. The product which started separating during the addition was stirred 10 minutes longer in the ice bath, filtered and washed with a little cold acetone: yield 13g of pale yellow solid, m.p. 203-204° (lit.[28] m.p. 205-207°).

Preparation of 3-morpholino-1-phenylpropene-1-thione[2]: A solution of 3-phenyl-1,2-dithioleum hydrogen sulfate (2.8g, 0.01 mol) and morpholine (1.7g, 0.02 mol) in ethanol (30 ml) was refluxed for 30 minutes. The reaction mixture was cooled and filtered. 3-Morpholino-1-phenylpropene-1-thione so obtained was recrystallised from ethanol, m.p. 136°C (lit.[2] m.p. 136°C).

Preparation of N,N-dimethyl-N′-thiobenzoylformamidine(9)[29]:

A mixture of thiobenzamide (13.7g, 0.10 mol) and N,N-dimethylformamide dimethylacetal (16.0 ml) was stirred at room temperature for one hour. The volatile materials were removed under reduced pressure. Trituration of the residue with a small amount of cold ether gave 18.6g (97%) of 9 as reddish orange crystals, m.p. 57°C (lit.[29], m.p. 57-59°C).

Preparation of N,N-dimethyl-N′-phenylthiocarbamoylformamidine (11)[29]:

A mixture of 50.0g of phenyl thiourea and 100 ml of N,N-dimethylformamide dimethylacetal was stirred at 100°C for one hour. On cooling to room temperature the reaction mixture deposited 67.4g (99%) of 11 as colourless crystals m.p. 153°C (lit.[29] m.p. 154-56°C).

General procedure for the preparation of N-arylbenzimidoyl chlorides (10)[30]:

A mixture of two equivalents of thionyl chloride and one equivalent of benzanilide was heated to reflux for 30 minutes. The excess of thionyl chloride was removed and the residue extracted with dry petroleum ether. The removal of petroleum ether yielded N-phenylbenzimidoyl chloride.

Similar procedure was followed for the preparation of N-p-chlorophenyl, N-m-chlorophenyl, N-o-chlorophenyl, N-p-bromophenyl and N-p-tolyl benzimidoyl chlorides.

General procedure for the reactions of 3-dimethylamino-1-arylpropene-1-thione with isonitriles:

A mixture of 3-dimethylamino-1-phenylpropene-1-thione (1a) (0.5g, 0.0026 mol) and phenyl isonitrile (2a) (0.3g, 0.0029 mol) was refluxed in dry dioxane for four hours. The solvent was removed under reduced pressure and the product so obtained (0.4g, 70%) was recrystallised from ethanol and characterised as 3a; m.p. 102°C (lit.[31], m.p. 105-6°C); IR(ν_{max}); 1640, 1580, 1480 cm^{-1}. Anal. found: N,5.54%; Calc. for $C_{15}H_{13}NS$; N,5.86%; MS; M/z 239(M^+).

Reactions of all other isonitriles (2) with 1 were carried out in a similar manner and the products are listed in the tables (1 and 2).

General procedure for the reactions of 3-morpholino-1-phenylpropene-1-thione (7) with N-arylisothiocyanates:

A solution of 3-morpholino-1-phenylpropene-1-thione (7) (0.4g, 0.0017 mol) and N-phenylisothiocyanate (0.25g, 0.0018 mol) in dry acetonitrile (15 ml) was refluxed for a period of five hours. The solid obtained 0.4g (87%) after the removal of the solvent under reduced pressure was recrystallised from a mixture (1:1) of benzene and hexane and characterised as N-(N-phenylthiocarbamoyl) morpholine (8), m.p. 128°C (lit.[32] m.p. 130.5°C). Mass calculated for $C_{11}H_{14}N_2OS$; 222; Found: 222; ^1H NMR δppm ($CDCl_3$): 3.70(s,8H,-N⟨O⟩), 7.74(m,5H,Ar-H) and 7.50(b,1H,NH).

The reactions of 3-morpholino-1-phenylpropene-1-thione with other N-arylisothiocyanates were carried out by following the same procedure (Tables 3 and 4).

General procedure for the reactions of N.N-dimethyl-N'-thiobenzoylformamidine (9) with N-arylbenzimidoyl chlorides (10):

To a stirred solution of 9 (0.7g, 0.0036 mol) in dry chloroform (30 ml) was added N-phenylbenzimidoyl chloride (10a) (0.86g, 0.0040 mol) and the reaction mixture was stirred at room temperature for one hour. The residue obtained after careful removal of the solvent under reduced pressure was stirred with aquous ethanol (75%). The solid thus obtained (1.15g, 82%) was recrystallised from a mixture (1:1) of benzene and hexane and characterised as dibenzimidoyl sulfide (12a); m.p. 199-200°C (lit.[33] m.p. 202-4°C); IR(ν_{max}): 1625, 1495, 1360 cm^{-1}. Anal. found C,79.13; H,5.21; N,7.04; Calc. for $C_{26}H_{20}N_2S$: C, 79.59; H,5.10; N,7.14%; MS; m/z 392 (M^+).

Reactions of all other N-arylbenzimidoyl chlorides (10) with 9 were carried out in a similar manner (Tables 5 and 6).

General procedure for the reactions of N,N-dimethyl-N'-phenylthiocarbamoylformamidine (11) with 10 :

A mixture of 11 (0.7g, 0.0030 mol) and 10a (0.86g, 0.0040 mol) in dry tetrahydrofuran (25 ml) was refluxed for five hours. Removal of the solvent under reduced pressure

resulted in a product mixture which was chromatographed over a silica gel column. Elution of the column with a mixture (1:1) of benzene and hexane gave thiobenzanilide (16) (0.39g, 65%) which was recrystallised from ethanol; m.p. 100°C (lit.[34] m.p. 101-102°C). Anal. found: C,73.70; H,5.22; N,7.00; Calc. for $C_{13}H_{11}NS$; C,73.24; H,5.16; N, 6.57%; MS: m/z 213(M^+). Further elution of the column with 1:1 mixture of benzene and hexane mixture gave a compound (0.3g, 33%) which was recrystallised from a mixture (1:1) of benzene and hexane and characterised as N,N'-diphenyl-benzamidine (15a); m.p. 143-44°C (lit.[35],m.p. 144°C); IR (ν_{max}): 3300, 1595 cm^{-1}. Anal. found: C, 83.84; H,5.93; N,10.24%; Calc. for $C_{19}H_{16}N_2$: C,83.82; H,5.88; N,10.29%); MS: m/z 272(M^+).

The same procedure was followed for the isolation of the products from the reactions of all other N-arylbenzimidoyl chlorides (10) with 11. The characterization data for the products is listed in Tables 7 and 8.

Table 1: Physical and analytical data for compounds (3a-3k)

Compound	R	R_1	m.p. °C (lit.m.p.) °C	Yield %	Mol.formula (M^+)	N% Calc.	N% Found
3a	H	C_6H_5	102 (105-106)[31]	70	$C_{15}H_{13}NS$ (239)	5.86	5.54
3b	$-CH_3$	C_6H_5	124	72	$C_{16}H_{15}NS$ (253)	5.53	5.45
3c	-Cl	C_6H_5	128	78	$C_{15}H_{12}ClNS$ (273)	5.12	4.93
3d	-Br	C_6H_5	135	80	$C_{15}H_{12}BrNS$ (318)	4.40	3.98
3e	H	CH_2-C_6H_5	71	62	$C_{16}H_{15}NS$ (253)	5.53	5.31
3f	-Cl	CH_2-C_6H_5	85	70	$C_{16}H_{14}ClNS$ (287)	4.87	4.66
3g	-Br	CH_2-C_6H_5	80	68	$C_{16}H_{14}BrNS$ (332)	4.22	3.82
3h	H	Cyclohexyl	105	68	$C_{15}H_{19}NS$ (245)	5.71	5.61

Table 1 (Contd....

3i	$-CH_3$	Cyclohexyl	100	75	$C_{16}H_{21}NS$ (259)	5.40	4.95
3j	-Cl	Cyclohexyl	100	72	$C_{15}H_{18}ClNS$ (279)	5.01	4.80
3k	-Br	Cyclohexyl	136	75	$C_{15}H_{18}BrNS$ (324)	4.32	4.16

Table 2: Spectral data for Compounds (3a-3k)

Compound	R	R_1	IR(KBr) ν_{max} cm^{-1}	^1H NMR($CDCl_3$) δppm
1	2	3	4	5
3a	H	C_6H_5	1630, 1585, 1490, 1230	6.62(d,1H_a), 7.10-7.90(m, 11H,Ar-H, and H_b), 15.20(b, 1H,NH)
3b	$-CH_3$	C_6H_5	1625, 1585, 1480, 1270	2.28(s,3H,CH_3), 6.58(d,1H_a), 7.10-7.85(m,10H,Ar-H and 1H_b), 15.20(b,1H,NH)
3c	-Cl	C_6H_5	1630, 1580, 1480, 1265	6.51(d,1H_a), 7.10-7.85(m, 10H,Ar-H and 1H_b), 15.20 (b,1H,NH)
3d	-Br	C_6H_5	1625, 1580, 1470, 1270	6.65(d,1H_a), 7.24-7.90(m, 10H,Ar-H and 1H_b), 15.40 (b,1H,NH)
3e	H	CH_2-C_6H_5	1610, 1585, 1498, 1260	4.50(d,2H,-CH_2-, J=6Hz), 6.50(d,1H_a), 7.23-7.85(m, 11H,Ar-H,1H_b), 14.90(b,1H, NH)
3f	-Cl	CH_2-C_6H_5	1625, 1585, 1500, 1265	4.59(d,2H,-CH_2-,J=6Hz),6.50 (d,1H_a), 7.30-7.90(m,10H, Ar-H,1H_b), 14.00(b,1H,NH)

Table 2 (Contd...)

1	2	3	4	5
3g	-Br	CH_2-C_6H_5	1610, 1580, 1498, 1275	4.53(d,2H,-CH_2-,J=6Hz), 6.46(d,1H_a), 7.20-7.66(m. 10H,Ar-H,1H_b), 13.56(b, 1H,NH)
3h	H	Cyclohexyl	1620, 1585, 1498, 1265	1.30-2.10(m,10H,Cyclohexyl), 3.29(m,1H,methine), 6.40 (d,1H_a), 7.15-7.85(m,6H, Ar-H,1H_b), 13.73(b,1H,NH)
3i	-CH_3	Cyclohexyl	1620, 1585, 1490, 1260	1.20-2.15(m,10H,Cyclohexyl), 3.23(m,1H,methine), 6.43 (d,1H_a), 7.00-7.50(m,5H, Ar-H,1H_b), 13.76(b,1H,NH)
3j	-Cl	Cyclohexyl	1620, 1580, 1490, 1260	1.12-2.15(m,10H,Cyclohexyl), 3.33(m,1H,methine), 6.30 (d,1H_a), 7.16-7.82(m,5H, Ar-H,1H_b), 13.86(b,1H,NH)
3k	-Br	Cyclohexyl	1610, 1580, 1490, 1250	1.10-2.20(m,10H,Cyclohexyl), 3.38(m,1H,methine),6.53(d, 1Ha),7.40-7.90(m,5H,Ar-H, 1H_b), 13.90(b,1H,NH)

Table 3: Physical and analytical data for compounds (8a-8e)

Compound	R	Yield %	m.p. °C	N% Calc.	N% Found	Molecular formula (M^+)
8a	H	86	128 (130.5)[32]	12.61	12.70	$C_{11}H_{14}N_2OS$ (222)
8b	$-CH_3$	83	138-140	11.86	12.01	$C_{12}H_{16}N_2OS$ (236)
8c	-Cl	70	145	10.94	10.97	$C_{11}H_{13}ClN_2OS$ (256)
8d	-OMe	83	102	11.11	10.90	$C_{12}H_{16}N_2O_2S$ (252)
8e	-OEt	76	166	10.52	10.76	$C_{13}H_{18}N_2O_2S$ (266)

Table 4: Spectral data for compounds (8a-8e)

Compound	R	IR(KBr) ν_{max} cm^{-1}	^1H NMR($CDCl_3$) δppm
8a	H	3200, 1600, 1540, 1220	3.7(s,8H,-N⬡O), 7.0-7.4(m, 5H,Ar-H), 7.5(b,1H,NH)
8b	$-CH_3$	3200, 1595, 1530, 1220	2.6(s,3H,$-CH_3$), 3.8(s,8H, -N⬡O), 7.0-7.4(m,4H,Ar-H), 7.6(b,1H,NH)
8c	-Cl	3200, 1600, 1535, 1220	3.9(s,8H,-N⬡O), 7.0-7.4(m, 4H,Ar-H), 7.8(b,1H,NH)
8d	-OMe	3200, 1610, 1540, 1240	3.9(s,3H,$-OCH_3$), 3.8(s,8H, -N⬡O), 6.8-7.2(m,4H,Ar-H), 7.4(b,1H,NH)
8e	-OEt	3200, 1610, 1540, 1240	1.4(t,3H,-C-CH_3), 4.0(q,2H, $-OCH_2-$), 3.8(s,8H,-N⬡O), 6.8-7.4(m,5H,Ar-H),NH)

Table 5: Physical and analytical data for dimidoyl sulfides (12a-f)

Compound	R	m.p. (lit.m.p.) °C	ref	Yield %	Mol. formula (M^+)		Calc.	Found
12a	H	199-200 (202-4)	33	82	$C_{26}H_{20}N_2S$ (392)	C	79.59	79.13
						H	5.10	5.21
						N	7.14	7.04
12b	p-CH_3	138		80	$C_{28}H_{24}N_2S$ (420)		80.00	79.32
							5.71	5.80
							6.67	6.23
12c	o-Cl	123-24		79	$C_{26}H_{18}Cl_2N_2S$ (461)		67.68	67.44
							3.90	3.82
							6.07	5.91
12d	m-Cl	101		76	$C_{26}H_{18}Cl_2N_2S$		67.68	67.05
							3.90	3.72
							6.07	5.93
12e	p-Cl	145		81	$C_{26}H_{18}Cl_2N_2S$		67.68	66.90
							3.90	3.84
							6.07	6.21
12f	p-Br	175		78.5	$C_{26}H_{18}Br_2N_2S$		56.72	57.00
							3.27	3.12
							5.09	5.33

Table 6: Spectral data for dimidoyl sulfides (12a-f)

Compound	R	IR(KBr) ν_{max} cm^{-1}	^1H NMR($CDCl_3$) δppm
12a	H	1625, 1350	6.8-7.5(m,20H,Ar-H)
12b	p-CH_3	1625, 1345	2.19(s,6H,$2CH_3$), 6.8-7.5(m,18H,Ar-H)
12c	o-Cl	1625, 1350	6.8-7.5(m,18H,Ar-H)
12d	m-Cl	1625, 1350	6.8-7.5(m,18H,Ar-H)
12e	p-Cl	1625, 1350	6.8-7.5(m,18H,Ar-H)
12f	p-Br	1625, 1350	6.8-7.5(m,18H,Ar-H)

Table 7: Physical and analytical data for anilides (16) and N-aryl-N'-phenylbenzamidines (15)

Compound	R	m.p. (lit.m.p.) ref °C	Yield %	Mol.formula (M^+)	Analysis % Calc.	Found
16a	H	100 (101-102)[34]	65	$C_{13}H_{11}NS$ (213)	C 73.24	73.70
					H 5.16	5.22
					N 6.57	7.00
16b	p-CH_3	127 (128-29)[36]	68	$C_{14}H_{13}NS$ (227)	74.00	74.73
					5.73	5.71
					6.17	6.40
16c	P-Cl	147-48 (149)[37]	75	$C_{13}H_{10}NSCl$ (247)	63.03	63.24
					4.05	4.12
					5.66	5.69
16d	p-Br	142	72	$C_{13}H_{10}BrNS$ (292)	53.42	53.51
					3.42	3.48
					4.79	4.82
15a	H	143-44 (144)[35]	33	$C_{19}H_{16}N_2$	83.82	83.84
					5.88	5.93
					10.29	10.24
15b	p-CH_3	131 (133)[38]	30	$C_{20}H_{18}N_2$	83.92	84.01
					6.29	6.32
					9.79	9.91

Table 8: Spectral data for thiobenzanilides 16

Compound	R	IR(KBr) ν_{max} cm^{-1}	^1H NMR($CDCl_3$) δppm
16a	H	3300, 1630, 1590, 1225	9.2(b,1H,NH), 6.8-7.5 (m,10H,Ar-H)
16b	p-CH_3	3200, 1600, 1525, 1220	2.29(s,3H,CH_3), 9.13 (b,1H,NH,Ar-H)
16c	p-Cl	3160, 1600, 1520, 1220	9.16(b,1H,NH), 6.8-7.5 (m,9H,Ar-H)
16d	p-Br	3160, 1600, 1520, 1220	9.13(b,1H,NH), 6.8-7.5 (m,9H,Ar-H)

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