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

By

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A THESIS
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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

North-Eastern Hill University
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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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Parag Dhar Baruah

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CONTENTS

PREFACE

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.

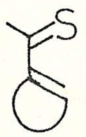
The entire documentation in this thesis is supported by appropriate references.

CHAPTER I

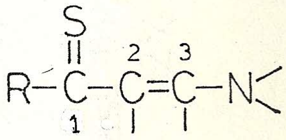
INTRODUCTION

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 β-aminovinylthioketones 2 are examples of this and are

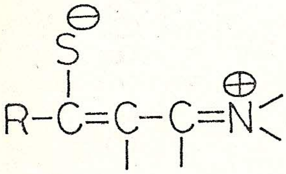


1



$$\mathrm{R}-\underset{1}{\overset{\overset{S}{\|}}{C}}-\underset{|}{\overset{2}{C}}=\underset{|}{\overset{3}{C}}-\mathrm{N}<$$

2a



$$\mathrm{R}-\overset{\overset{S^{\ominus}}{|}}{C}=\underset{|}{C}-\underset{|}{C}=\overset{\oplus}{\mathrm{N}}<$$

2b

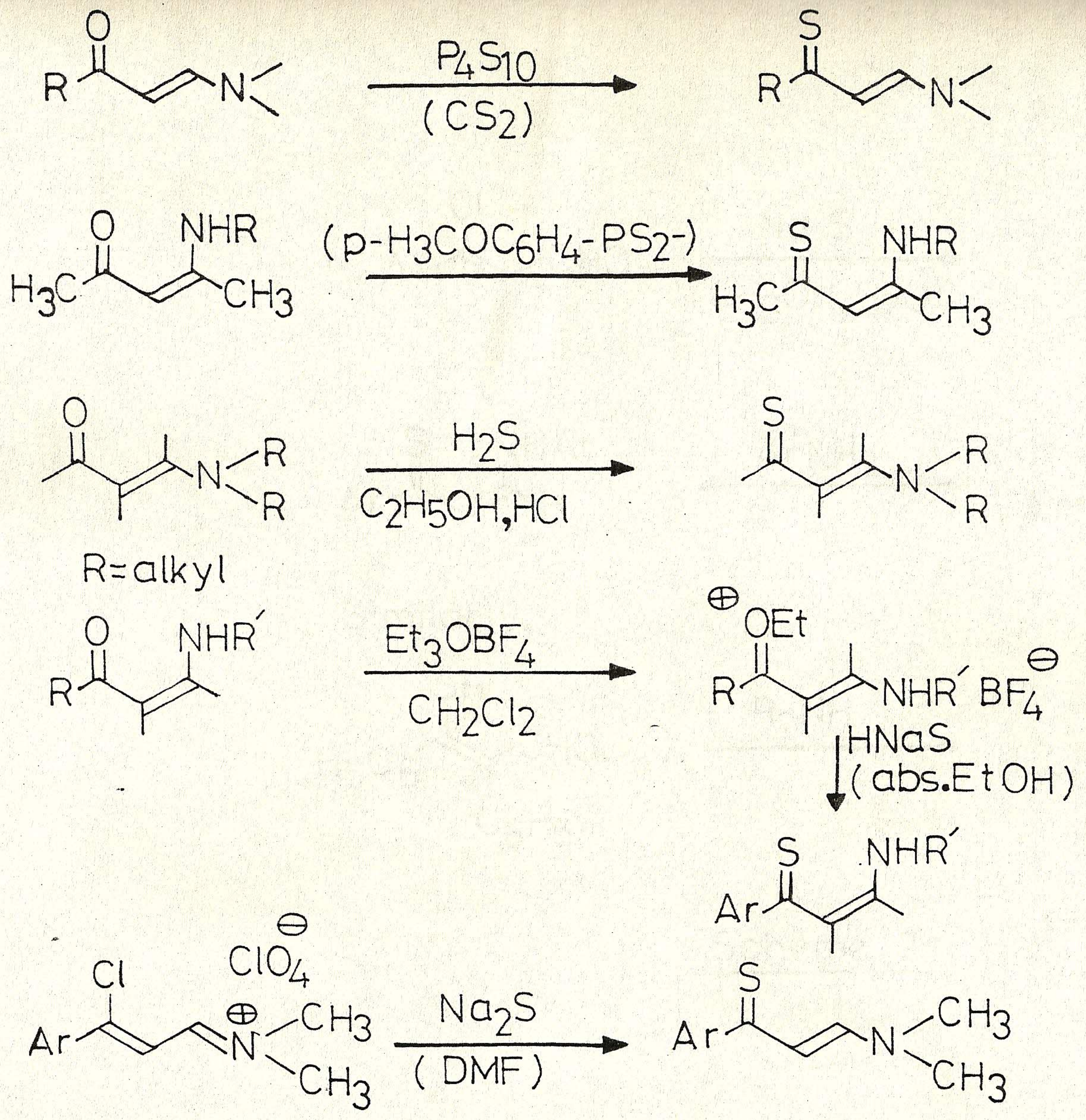
referred to as "thioamide vinylogs" or "enamino-thiones" in this thesis.

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.

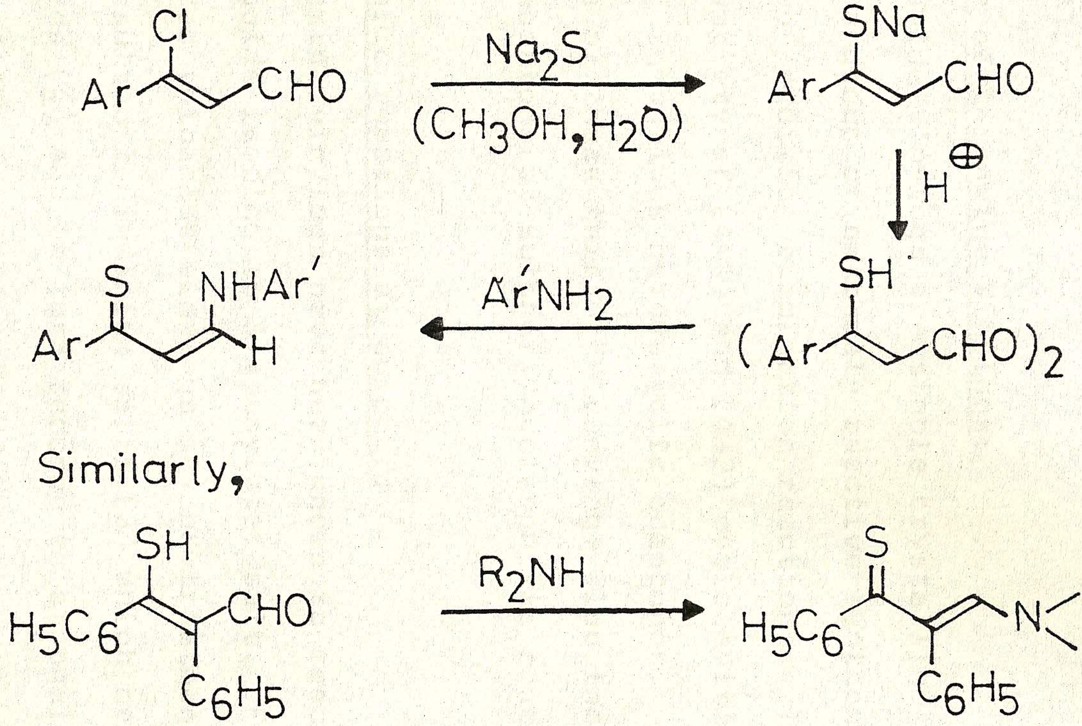
The second approach involves the reaction of an amine with ethylenic β-mercapto-aldehydes where the mercapto group is attached before condensation of the amine on the aldehyde[15-17] (Scheme 2).

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



Yield	Ref.
50%	3-6
20-74%	7
less than 12%	6, 8
30-60%	9-11
	12-14

Scheme 1


Cl
Ar
CHO
Na2S
(CH3OH, H2O)
SNa
Ar
CHO
H⊕
SH
(Ar
CHO)2
Ar′NH2
S
NHAr′
Ar
H
Similarly,
SH
H5C6
CHO
C6H5
R2NH
S
H5C6
N
R
R
C6H5

Scheme 2

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

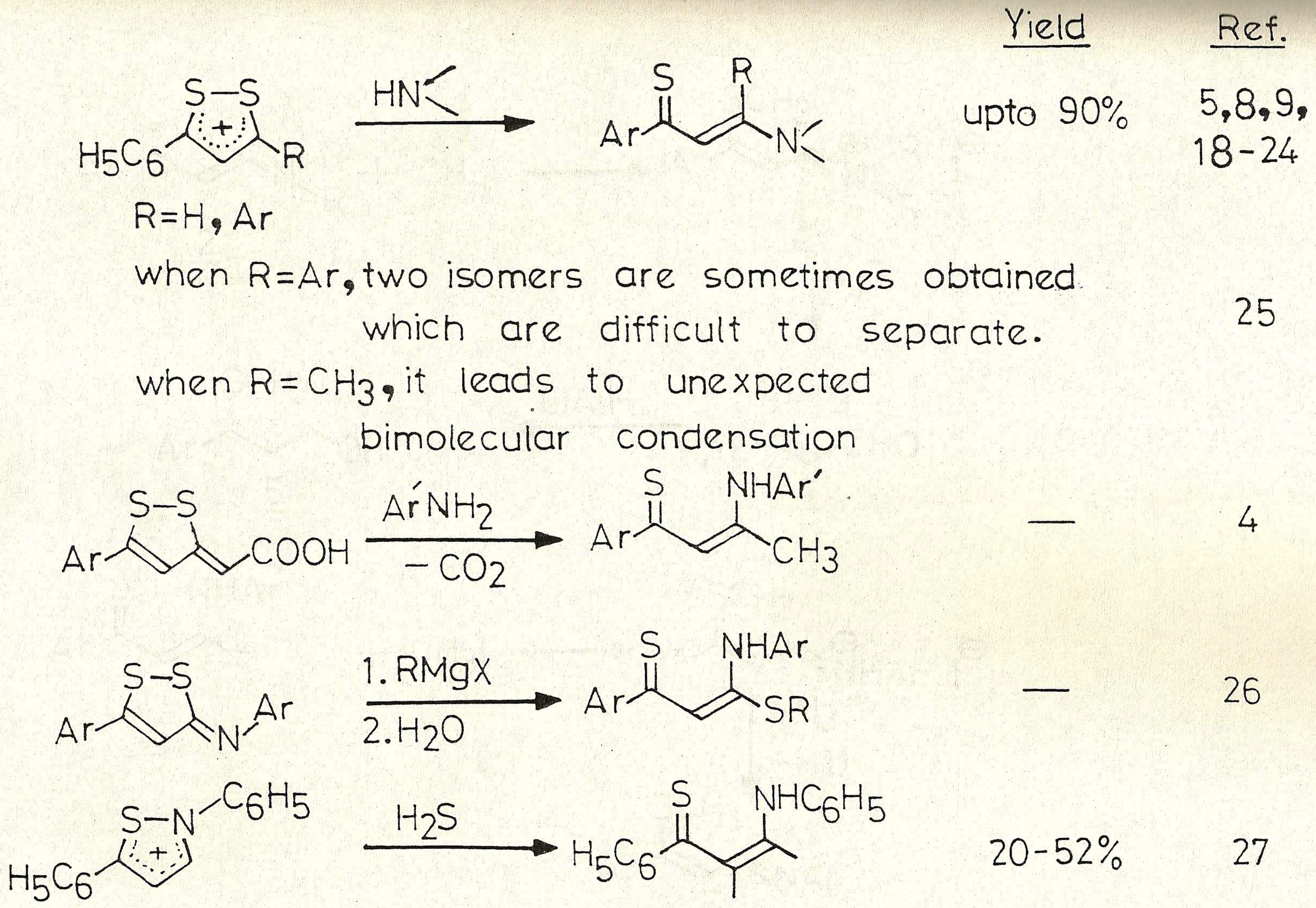
Reactions of thioamide Vinylogs:

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

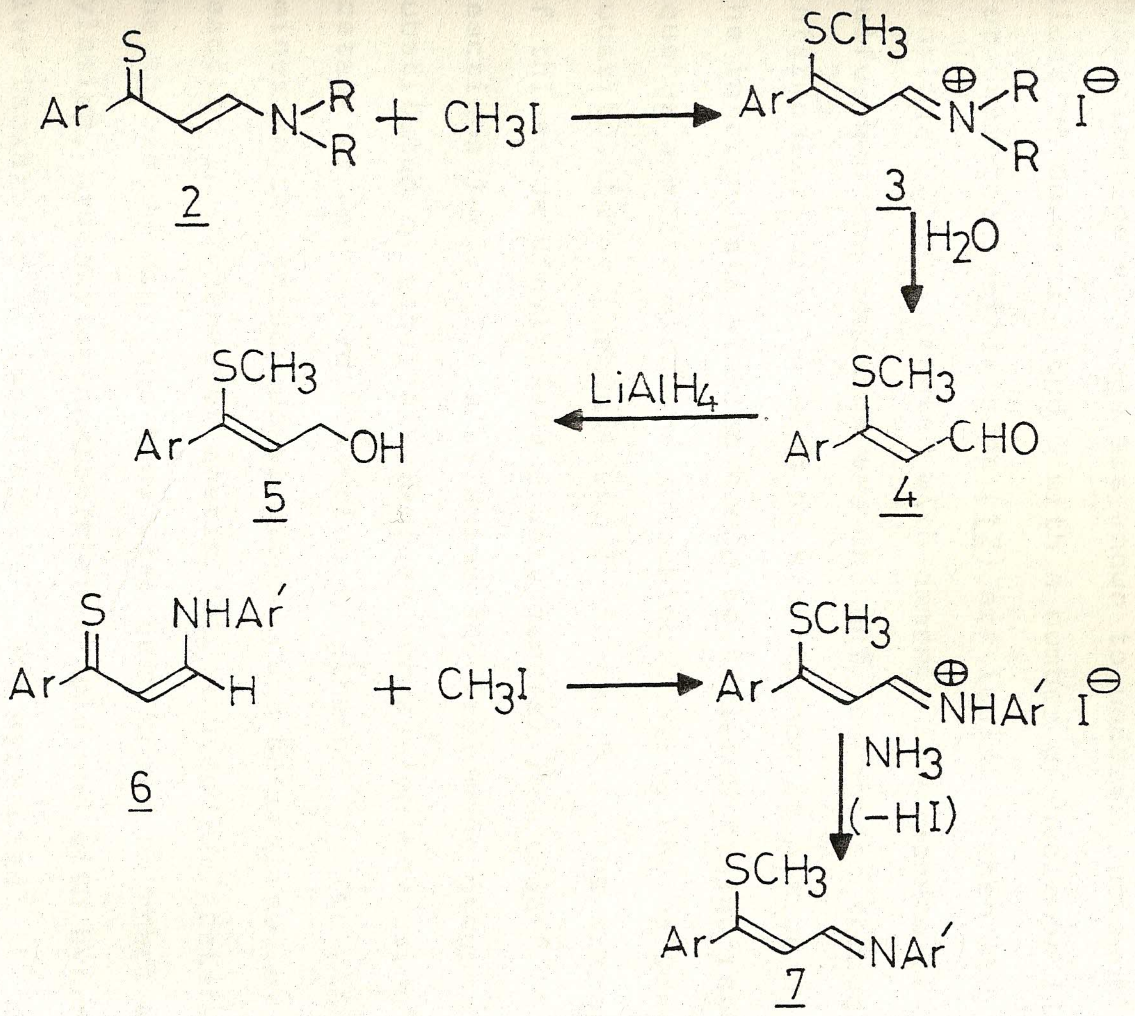


R=H, Ar

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

when R=CH_3, it leads to unexpected bimolecular condensation

Scheme 3



Ar
S
N
R
R
2
+ CH$_3$I
SCH$_3$
Ar
N$^{\oplus}$
R
R
I$^{\ominus}$
3
H$_2$O
SCH$_3$
Ar
CHO
4
LiAlH$_4$
SCH$_3$
Ar
OH
5
S
NHAr′
Ar
H
6
+ CH$_3$I
SCH$_3$
Ar
NHAr′$^{\oplus}$
I$^{\ominus}$
NH$_3$
(−HI)
SCH$_3$
Ar
NAr′
7

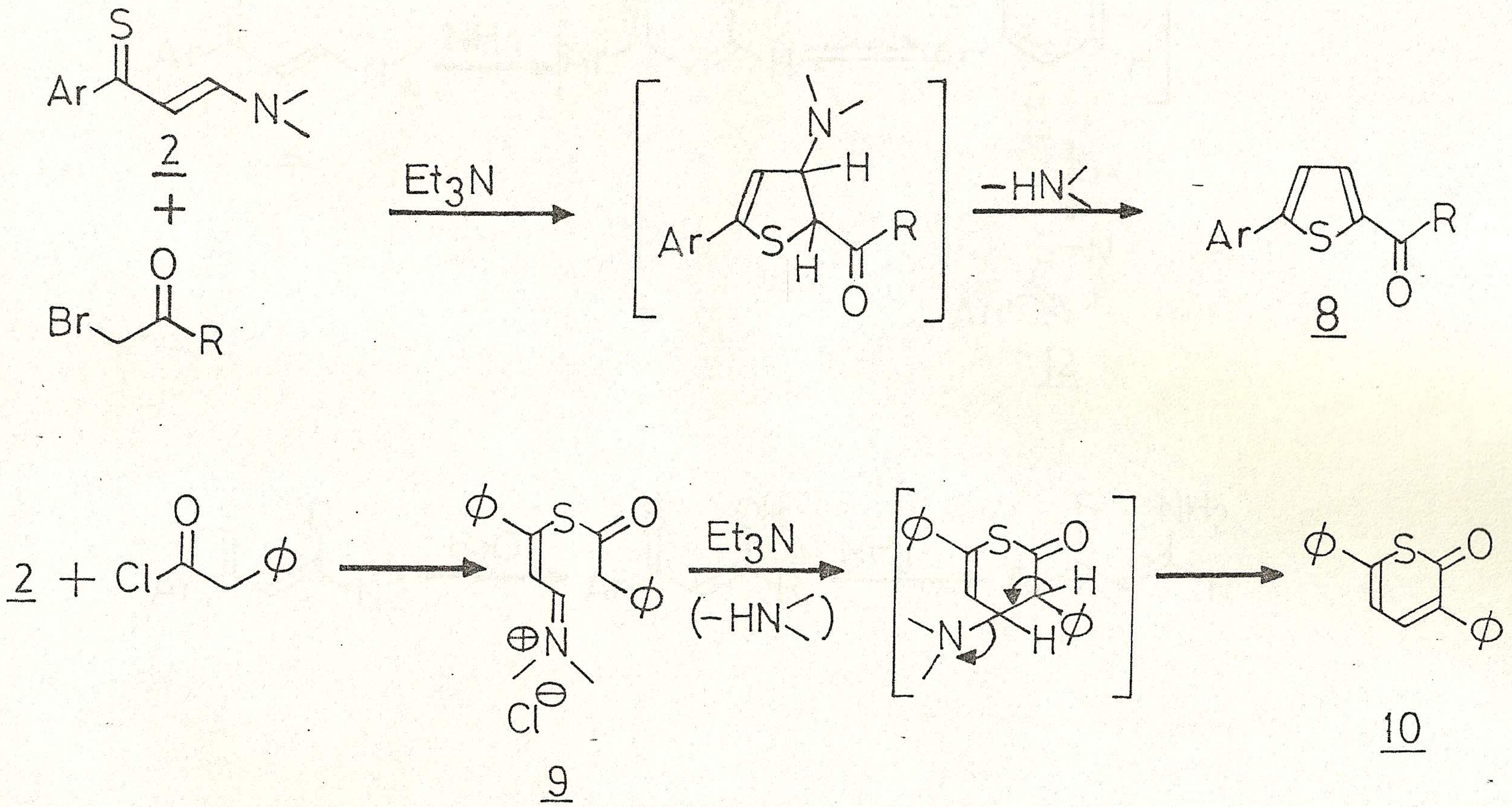
Scheme 4

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

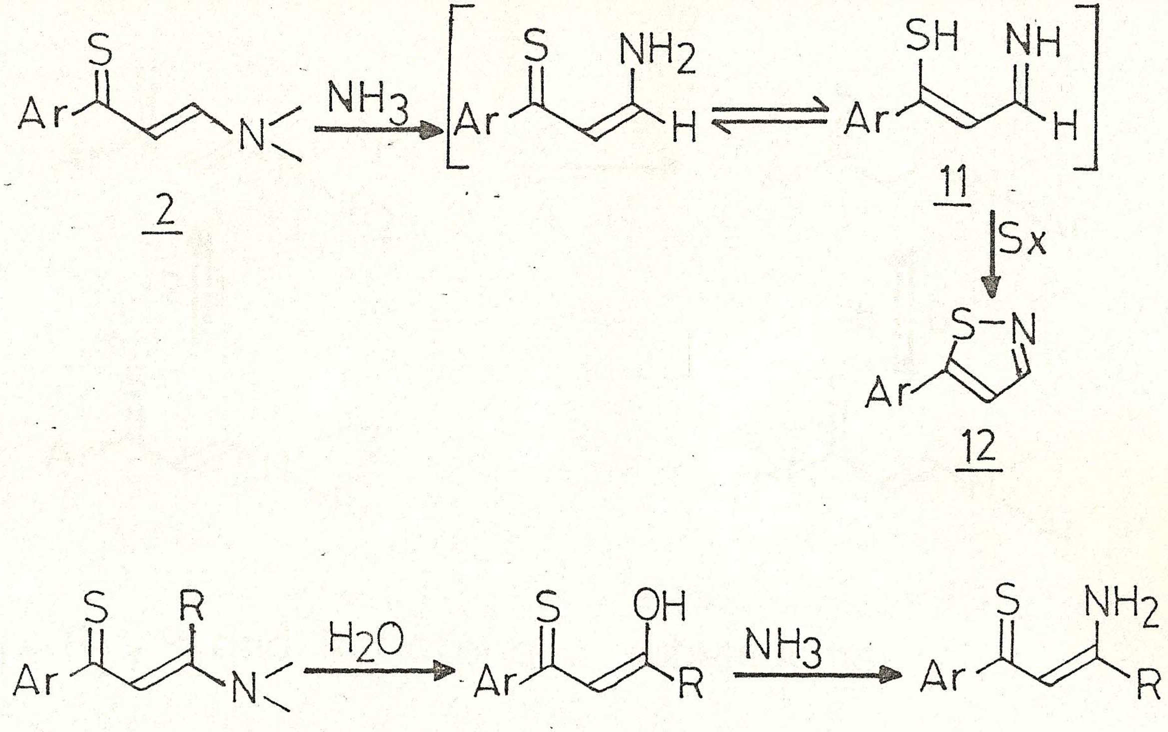
Nucleophilic reactions at carbons 1 and 3:

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.

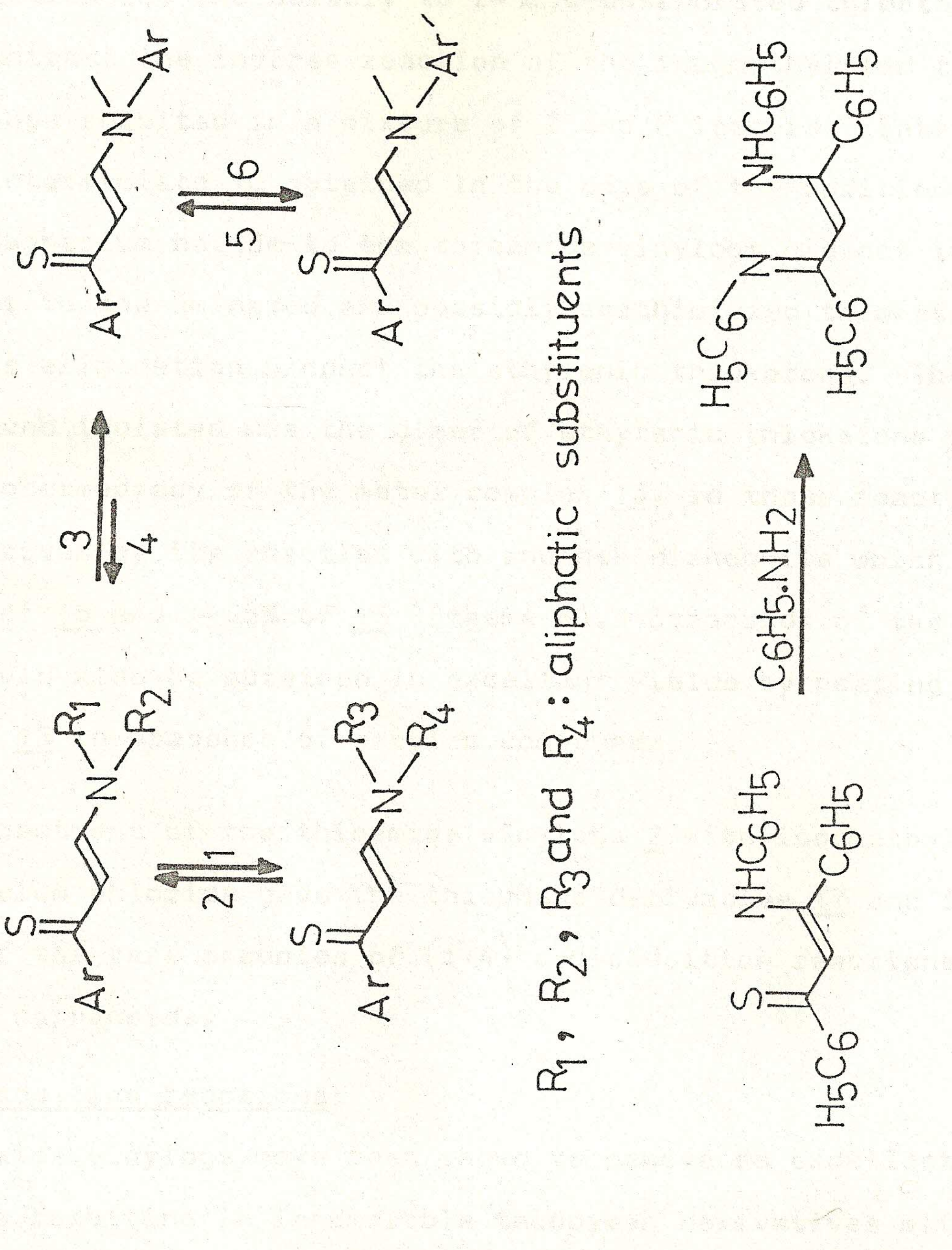
When the thioamide vinylogs are reacted with organomagnesium or organolithium compounds the nucleophilic attack at carbon 3



Scheme 5



Scheme 6


S
Ar
N
R1
R2
1
2
S
Ar
N
R3
R4
3
4
S
Ar
N
Ar
5
6
S
Ar
N
Ar'
R1, R2, R3 and R4 : aliphatic substituents
S
H5C6
NHC6H5
C6H5
C6H5.NH2
H5C6
N
H5C6
NHC6H5
C6H5

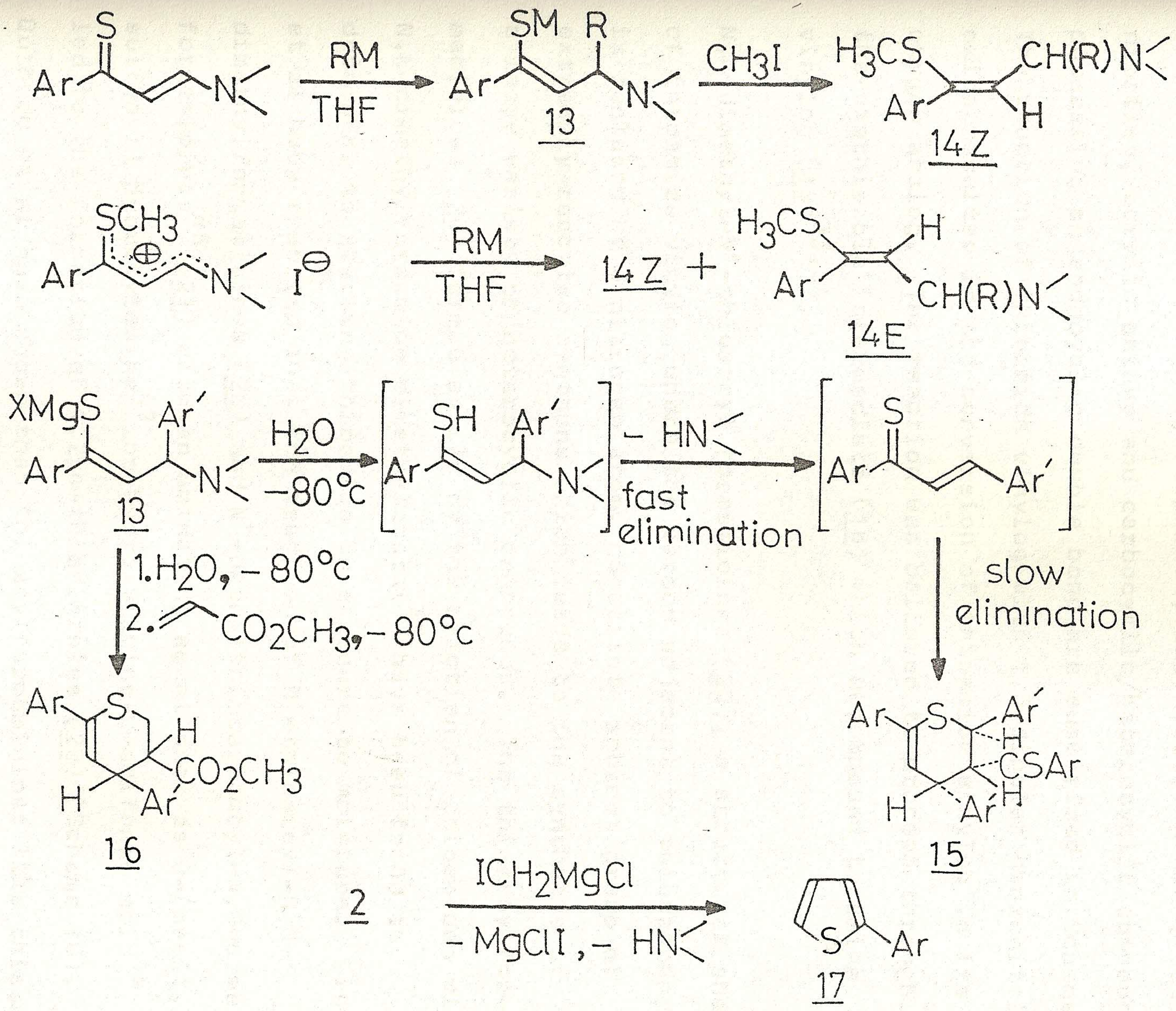
Scheme 7

of the vinylog at 0°C (or at -80°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,ß-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 ~9% of 16 and ~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 iodomethylmagnesium chloride gave the thiophene derivative 17 and is one of the rare examples of (1+4) cycloaddition reactions of metal carbenoids.

Cycloaddition reactions:

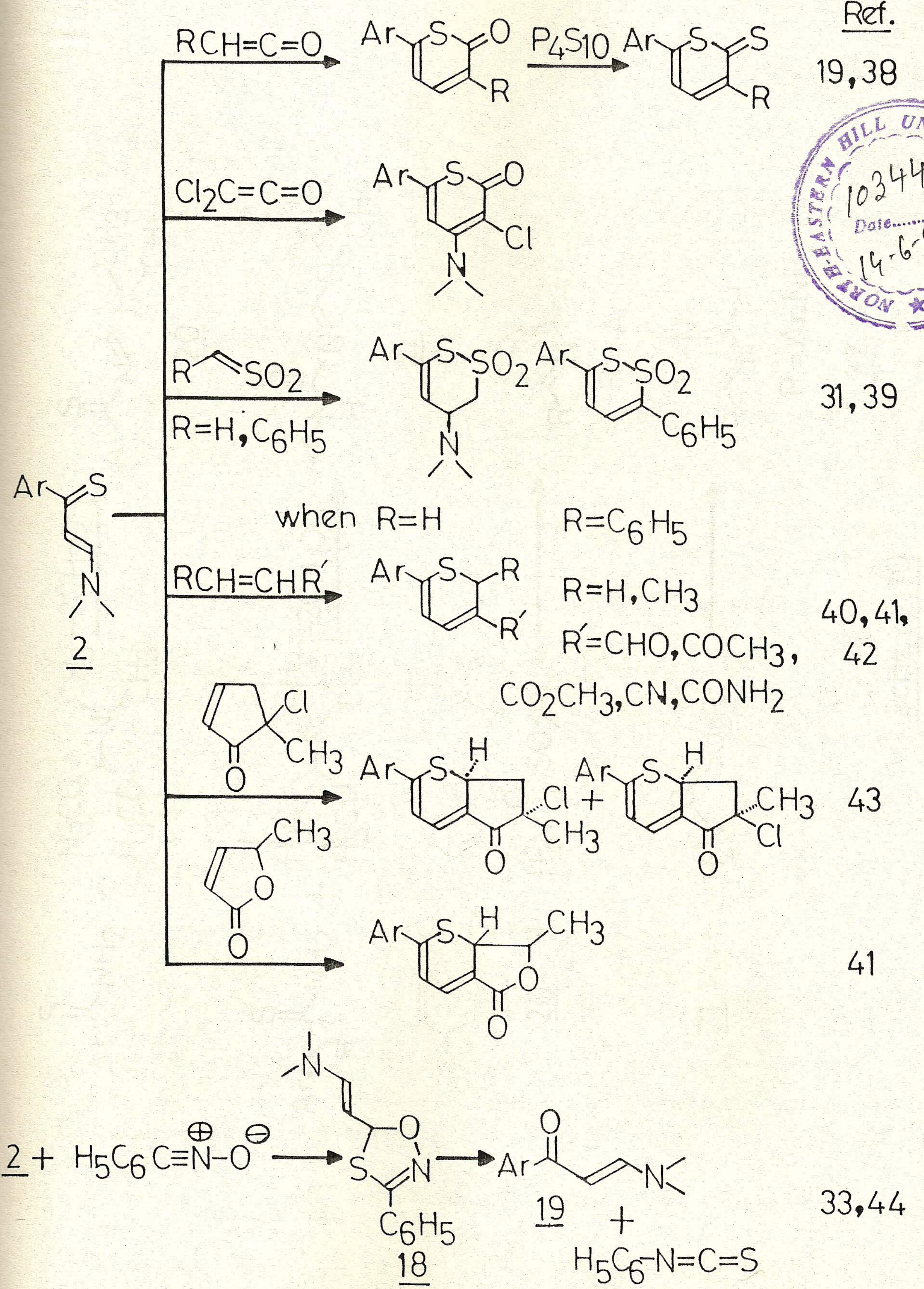
Thioamide vinylogs have been shown to behave as excellent heterodienes resulting in innumerable thiopyran derivatives with various


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

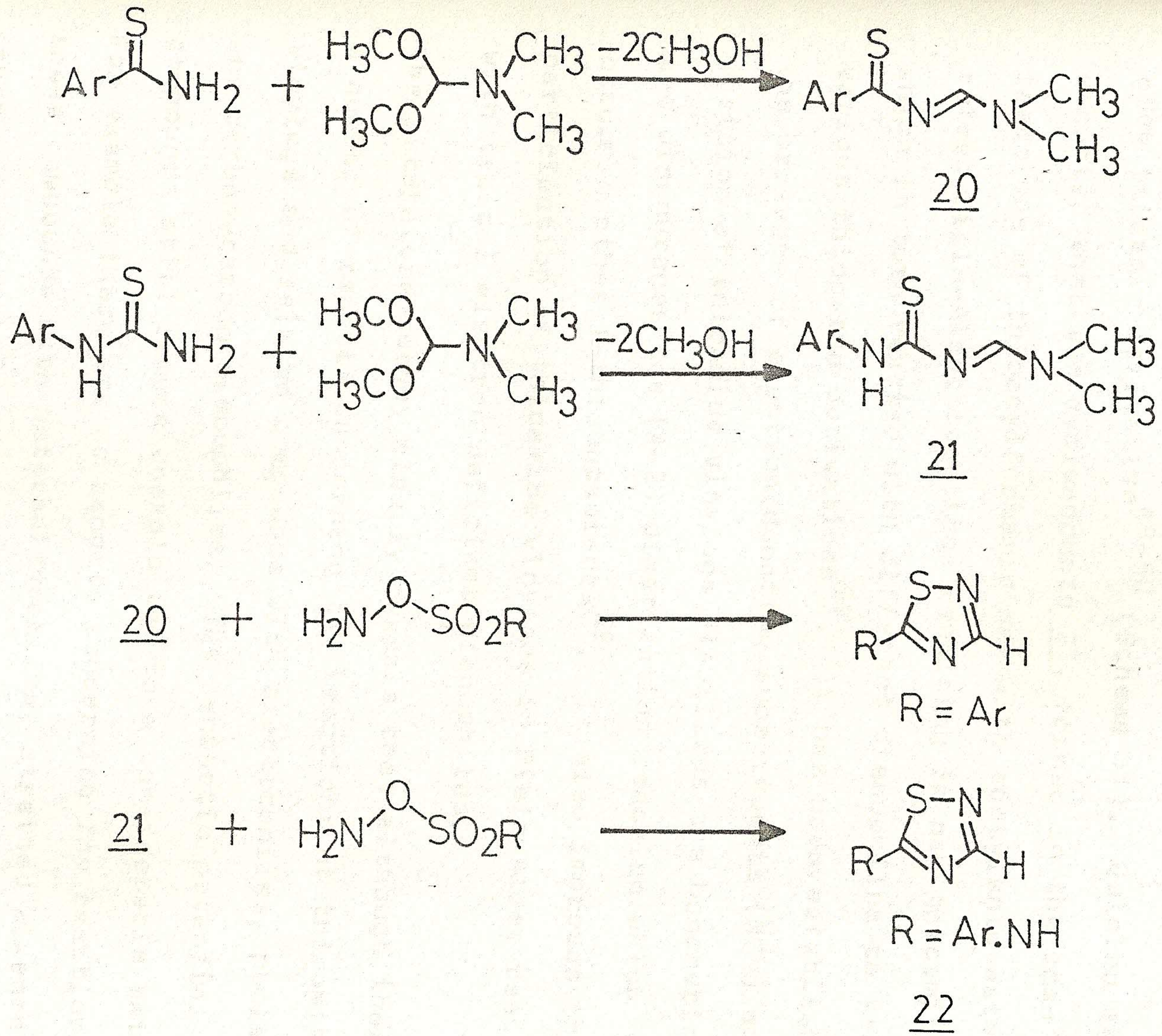
Scheme 8

dienophiles. Diels-Alder cycloaddition reactions of <u>2</u> with dienophiles like ketenes, sulphenes, aldehydes, ketones, esters, nitriles, acrylic amides and carbocyclic/heterocyclic compounds possessing an endocyclic double bond are summarised in Scheme <u>9</u>. 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 (<u>18</u>) which decomposed to amide vinylog (<u>19</u>)[33,34].

N,N-dimethyl-N′-thioaroyl formamidines (<u>20</u>), 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 (<u>20</u>) 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 (<u>20</u>) and N′-phenylthiocarbamoyl-N,N-dimethylformamidines[46] (<u>21</u>) 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 (<u>22</u>) (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
Ar
S
O
R
P4S10
S
19,38
Cl2C=C=O
Cl
N
R SO2
R=H, C6H5
SO2
C6H5
31,39
when R=H
R=C6H5
RCH=CHR′
R′
R=H, CH3
R′=CHO, COCH3, CO2CH3, CN, CONH2
40,41, 42
CH3
H
43
41
2
18
19
H5C6-N=C=S
33,44

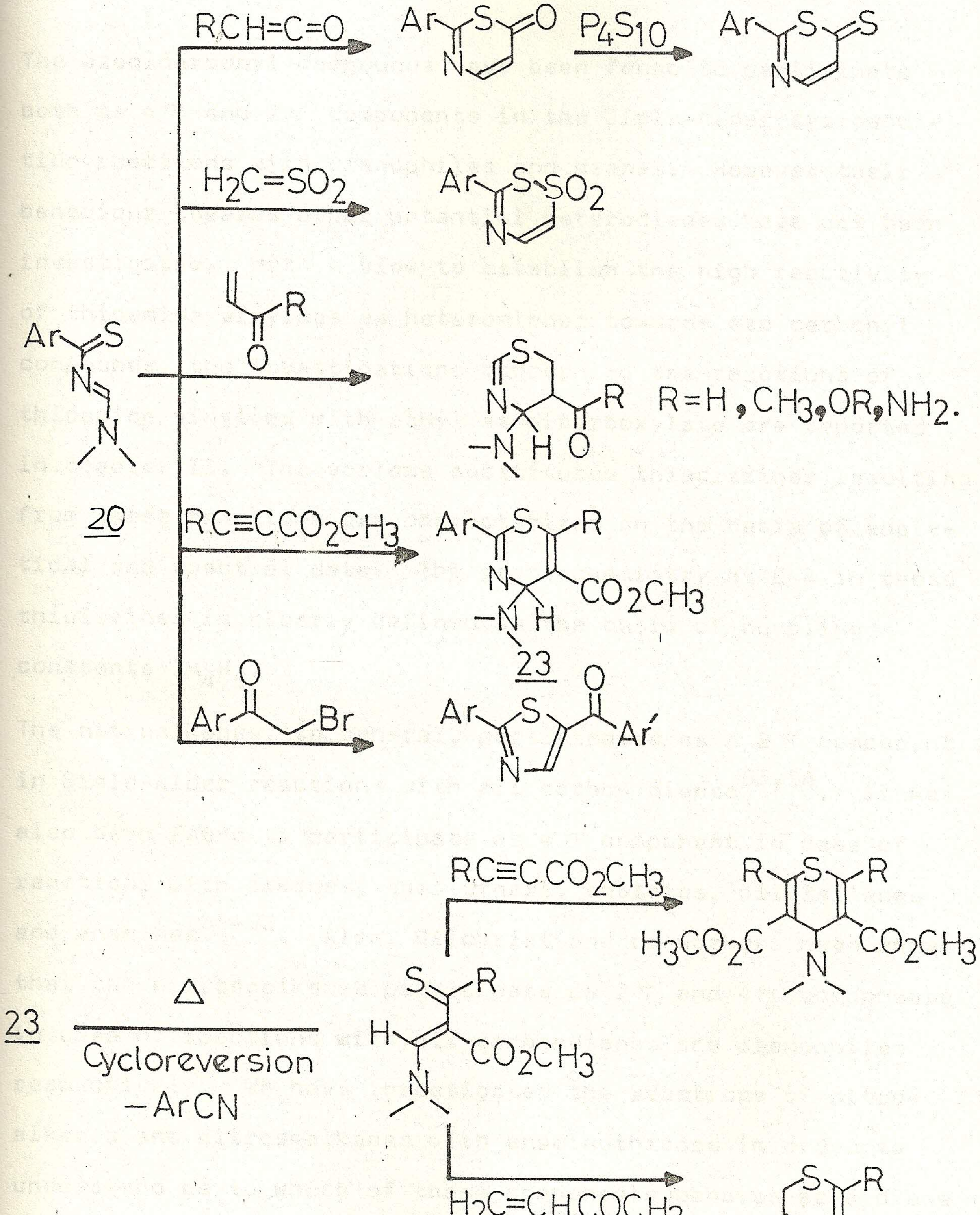
Scheme 9



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 ($\ddot{N}<$) 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.

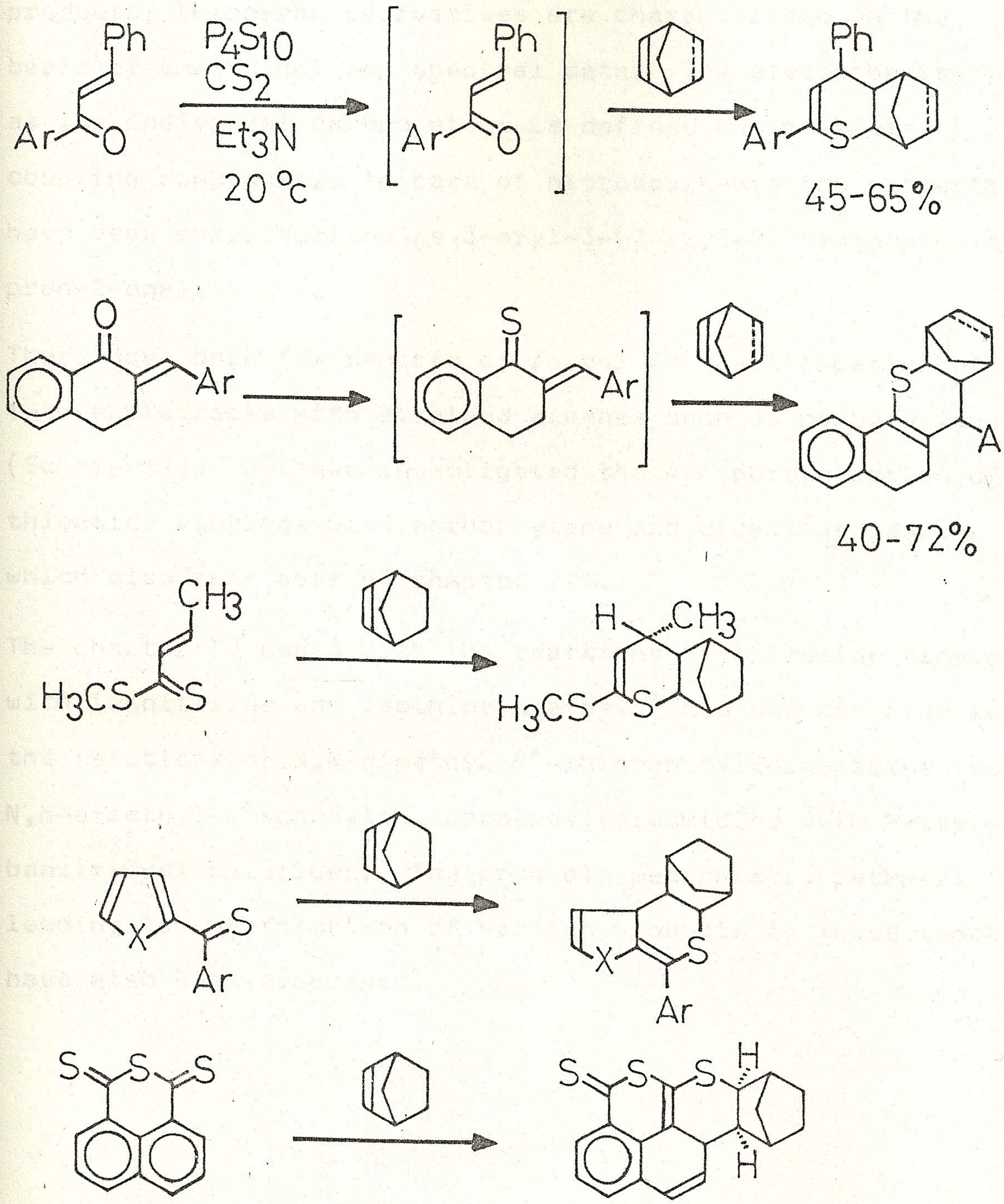
The literature survey clearly reveals that although there are a number of reports concerning the reactions of thioamide vinylogs and related compounds with electrophiles, nucleophiles and carbon-carbon dienophiles. The synthetic potential of these compounds still remain unexploited to a considerable 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=H, CH3, OR, NH2.
20
RC≡CCO2CH3
23
Ar
Br
23
Δ
Cycloreversion
−ArCN
RC≡C CO2CH3
H2C=CH COCH3
CO2CH3
H3CO2C

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


Ph
Ar
O
P_4S_{10}
CS_2
Et_3N
20 °C
Ph
Ar
O
Ph
Ar
S
45-65%
O
Ar
S
Ar
S
Ar
40-72%
CH_3
H_3CS
S
H
CH_3
H_3CS
S
X
S
Ar
X
S
Ar
S
S
S
S
S
S
H
H

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-arylbenzimidoyl chlorides. The probable mechanistic pathways leading to the formation of various products in these reactions have also been discussed.

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