INVESTIGATIONS ON OXOKETENE DITHIOACETALS : NEW CARBON - CARBON BOND FORMING REACTIONS AND THEIR FURTHER TRANSFORMATIONS TO NOVEL CARBOCYCLES AND HETEROCYCLES

By

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

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3.	Medicinal Chemistry	Chem - 631
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PREFACE

Polarized ketene dithioacetals which can be easily prepared from a variety of active methylene compounds have been extensively explored in this laboratory for the development of new synthetic methods for a variety of heterocyclic and carbocyclic compounds. The α-oxoketene dithioacetals have also shown to be versatile intermediates for stereo- and regioselective carbon-hydrogen and carbon-carbon bond forming reactions involving metal hydrides and organometallic reagents respectively. Some interesting transformations involving reactions of organometallic reagents with α-oxoketene dithioacetals have been investigated in the present study.

The first Chapter gives an account of some of the recent transformations of α-oxoketene dithioacetals reported from this laboratory. The second Chapter of the thesis describes the interesting results involving reactions of propargylmagnesium bromide with α-oxoketene dithioacetals. Subsequent Lewis acid transformations of the alcohols thus formed has resulted in the development of a new synthetic method for aromatic annelation of easily available aliphatic precursors. The mechanisms and the scope of these transformations are described in detail.

The third Chapter is divided into two parts: Part 1 describes the reactions of α-oxoketene dithioacetals with lithioacetonitriles and the part II describe the reactions of α-oxoketene dithioacetals with β-substituted-β-lithioaminoacrylonitriles. The products arising out of these reactions, their mechanism, scope and limitation of the methodology developed are described in detail in this Chapter.

The fourth Chapter describes the studies of Diels-Alder cycloadditions reactions on vinylketene dithioacetals. A new efficient method of preparation of vinylketene dithioacetals from α-oxoketene dithioacetals have also been described.

CHAPTER I

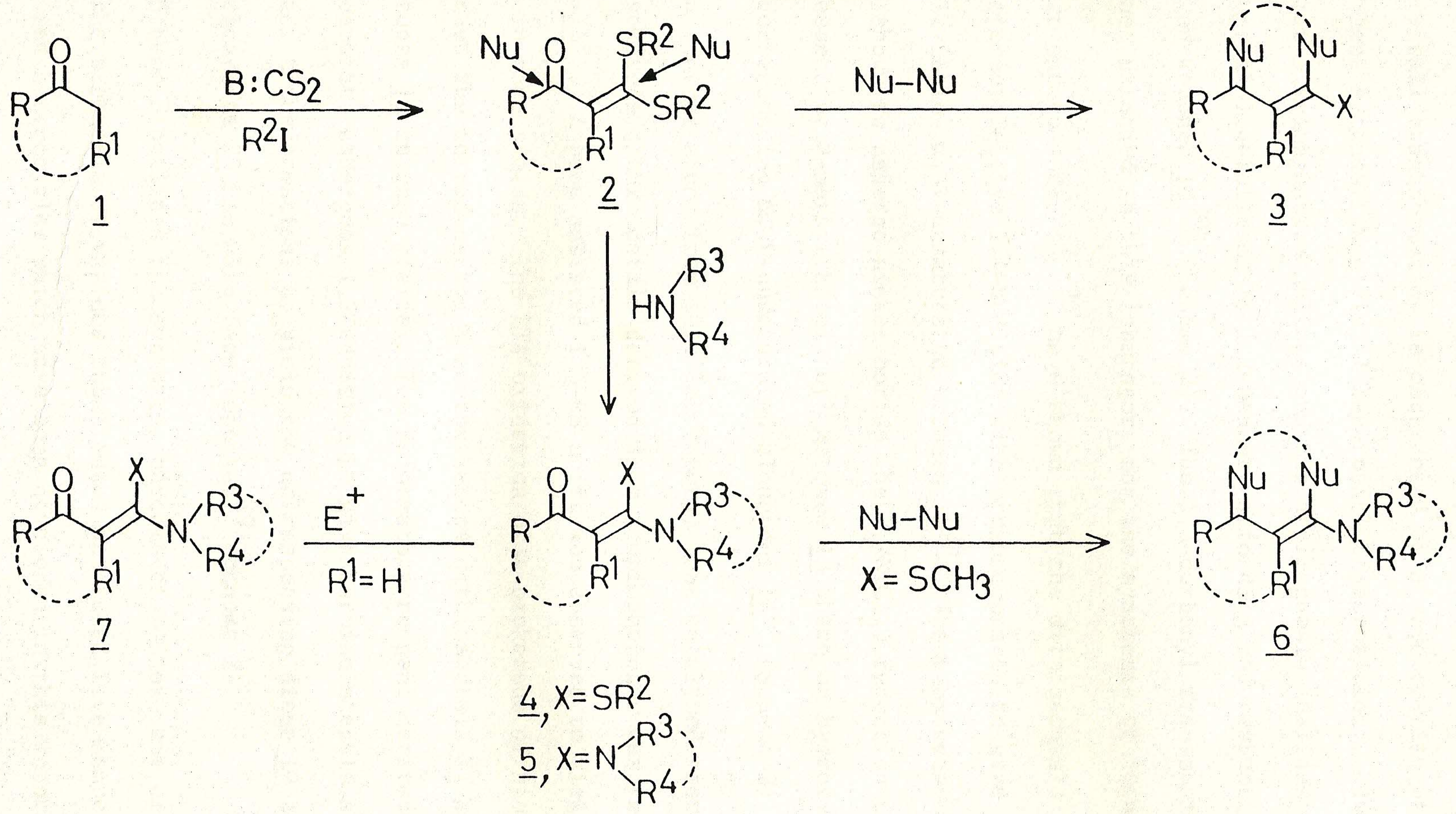
POLARIZED KETENE DITHIOACETALS: GENERAL INTRODUCTION

The α-oxoketene dithioacetals[1] are an important class of synthetic intermediates which can be prepared[2-10] by treating any active methylene compound of the general formula 1 with two equivalents of base and carbon disulphide followed by alkylation. The chemistry of α-oxoketene dithioacetals have been well documented[1,11]. They possess well defined physical properties and can be purified by any of the conventional purification methods. They are stable at room temperature and can withstand mild acidic and alkaline conditions. On the otherhand, the corresponding 0,0-acetals are moisture sensitive and undergo hydrolysis under mild conditions[11,12].

The first synthesis of α-oxoketene dithioacetal was reported by Kelber and co-workers in 1910[13-15]. However, the chemistry of these intermediates remained unexplored, until Thuillier and co-workers prepared these compounds in high yields in one pot reaction by reacting the active methylene ketones with carbon disulphide in the presence of base followed by alkylation[2-5]. Subsequently, several modifications have been made in choice of suitable bases maintaining the same conditions for obtaining higher yields of α-oxoketene dithioacetals[6-10].

The α-oxoketene dithioacetals can be visualized as masked β-ketoesters in which ester functionality is manifested as a ketene dithioacetal moiety. Alternatively, it may be considered as an α,β-unsaturated ketones containing a highly functionalized β-carbon. The α-oxoketene dithioacetals have been shown to be excellent 3-carbon fragments possessing 1,3-electrophilic centres with differing electrophilic properties, suitable for synthetic exploitation. They can further be converted to the corresponding ketene dihalogenides[16], S,N[17]- and N,N[18]-acetals making them more important precursors for a large variety of functionalized acetals. The α-oxoketene S,S-acetals, S,N- and N,N-acetals have been extensively used in this laboratory for developing a large number of new synthetic methods for both heterocyclic and carbocyclic systems (Scheme 1).

The carbonyl group of α-oxoketene dithioacetals have been shown to undergo sodium borohydride reduction to give the corresponding carbinolacetals which on subsequent acid catalysed treatment gave a number of rearranged products[19]. The 1,2-reduction of these intermediates was reinvestigated in our laboratory and the resulting carbinolacetals were shown to undergo smooth methanolysis in the presence of borontrifluoride etherate to afford highly regio-and stereoselective α,β-unsaturated methyl esters $\underline{8}$[20a], in high yields. Under controlled $BF_3.Et_2O$ catalysed hydrolysis the


R
O
R1
1
B:CS2
R2I
Nu
O
SR2
Nu
SR2
R1
2
Nu–Nu
Nu
Nu
X
R1
3
HN
R3
R4
O
X
R3
N
R4
R1
E+
R1=H
Nu–Nu
X = SCH3
7
6
4, X=SR2
5, X=N R3 R4

Scheme 1

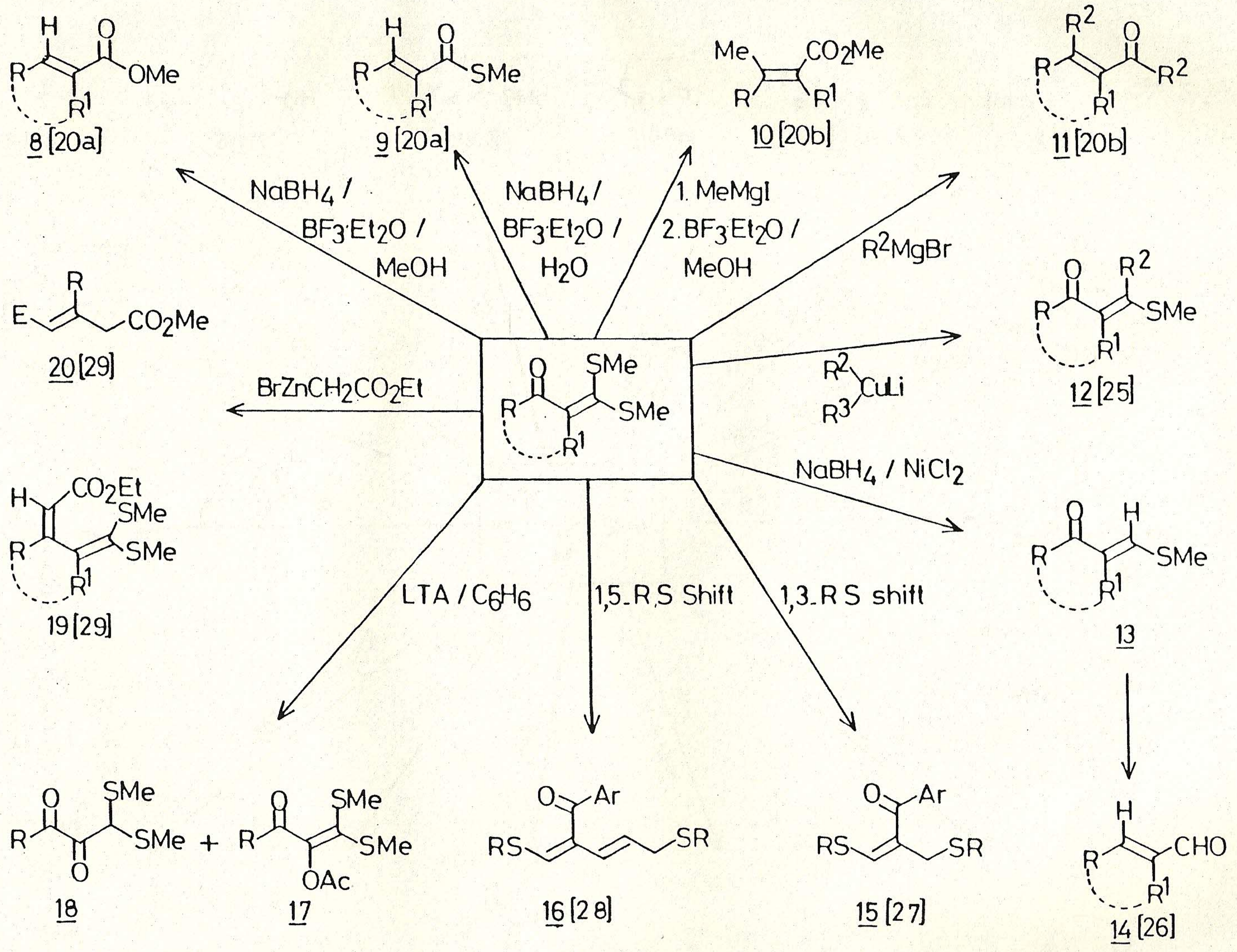
corresponding thiol ene esters 9[20a] were also obtained in high yields.

The overall transformation is considered as a homologation of active methylene ketenes, involving 1,3-carbonyl transposition. However, the bulkier alkylmagnesium halides and the arylmagnesium halides added in a sequential 1,4-followed by 1,2-manner, affording the respective α,β-unsaturated ketones 10[20b] (Scheme 2). The 1,3-carbonyl transposition was further extended in this laboratory for the synthesis of diene esters[21].

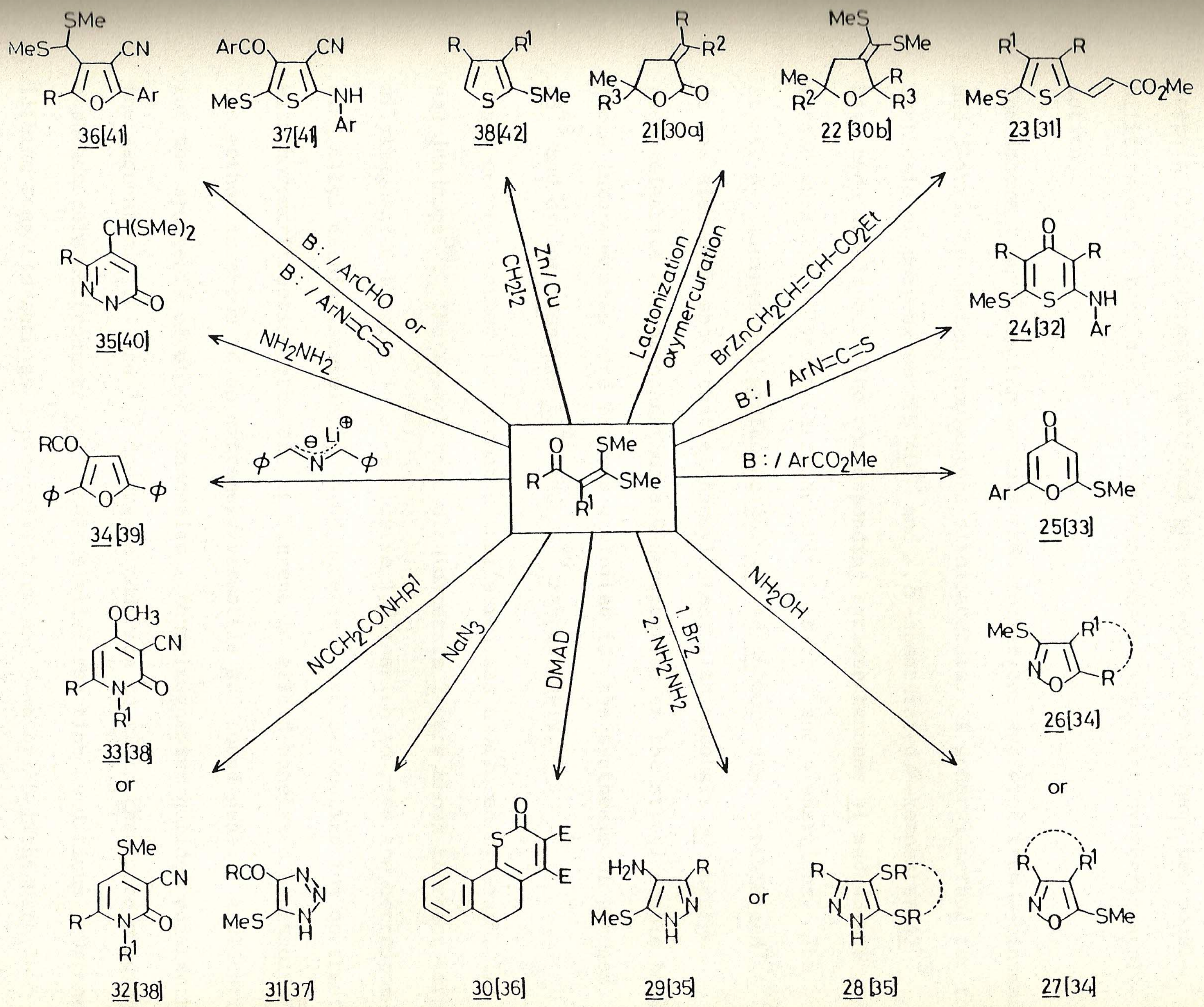
Dieter and co-workers[22-25] have shown that the dithioacetals 2 undergo chemo- and stereoselective 1,4-addition with organocuprates to give the corresponding β-alkylthio-α,β-unsaturated ketones 12[25]. The α-oxoketene dithioacetals were shown to undergo nickel boride ($NaBH_4/NiCl_2$) reduction to the corresponding β-methylthioalkenyl ketones 13 which on hydrolysis yielded the corresponding α,β-unsaturated aldehydes 14[26] (Scheme 2).

In an another study from this laboratory, base catalysed rearrangement of α-oxoketene dithioacetals derived from propiophenones was reported to give 15[27]. A base assisted 1,5-RS shift was observed to yield the dienes 16[28] in good yields. The LTA oxidation of α-oxoketene dithioacetals afforded the corresponding α-acetoxyketene dithioacetals 17 and the diketones 18 in good yields. The Reformatsky reagent derived from ethyl bromoacetate undergoes 1,2-addition to give carbinolacetals and their further transformations to yield the corresponding diene 19 and 1,3-propene dicarboxylate 20 has also been reported[29] (Scheme 2).

The Scheme 3 outlines the synthetic outcome of α-oxoketene dithioacetals for the synthesis of various substituted and fused five membered and six membered heterocycles which have been developed in this laboratory[30-42].


8 [20a]
9 [20a]
10 [20b]
11 [20b]
NaBH$_4$ / BF$_3$·Et$_2$O / MeOH
NaBH$_4$ / BF$_3$·Et$_2$O / H$_2$O
1. MeMgI 2. BF$_3$·Et$_2$O / MeOH
R^{2}MgBr
20 [29]
12 [25]
BrZnCH$_2$CO$_2$Et
R^{2}R^{3}CuLi
NaBH$_4$ / NiCl$_2$
19 [29]
13
LTA / C$_6$H$_6$
1,5-R,S Shift
1,3-R S shift
18
17
16 [28]
15 [27]
14 [26]

Scheme 2

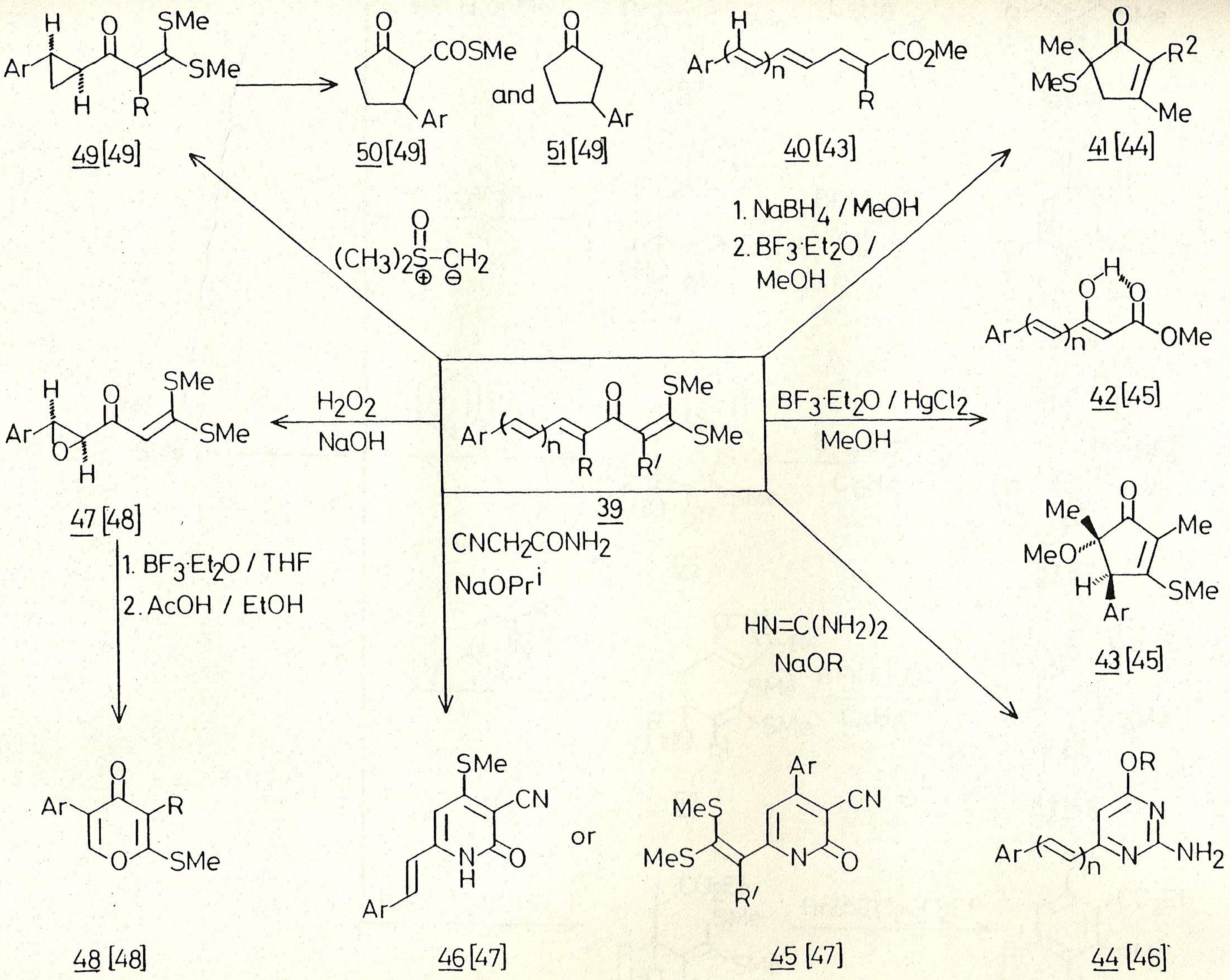

36[41]
37[41]
38[42]
21[30a]
22 [30b]
23[31]
35[40]
24[32]
34[39]
25[33]
33[38]
or
32[38]
31[37]
30[36]
29[35]
or
28[35]
26[34]
or
27[34]
B: / ArCHO or
B: / ArN=C=S
NH2NH2
Zn/Cu
CH2I2
Lactonization
oxymercuration
BrZnCH2CH=CH-CO2Et
B: / ArN=C=S
B: / ArCO2Me
NH2OH
1. Br2
2. NH2NH2
DMAD
NaN3
NCCH2CONHR1

Scheme 3

From these transformations it is apparent that the α-oxoketene dithioacetals with different functional groups would provide many new possibilities of further useful transformations of important synthetic applications.

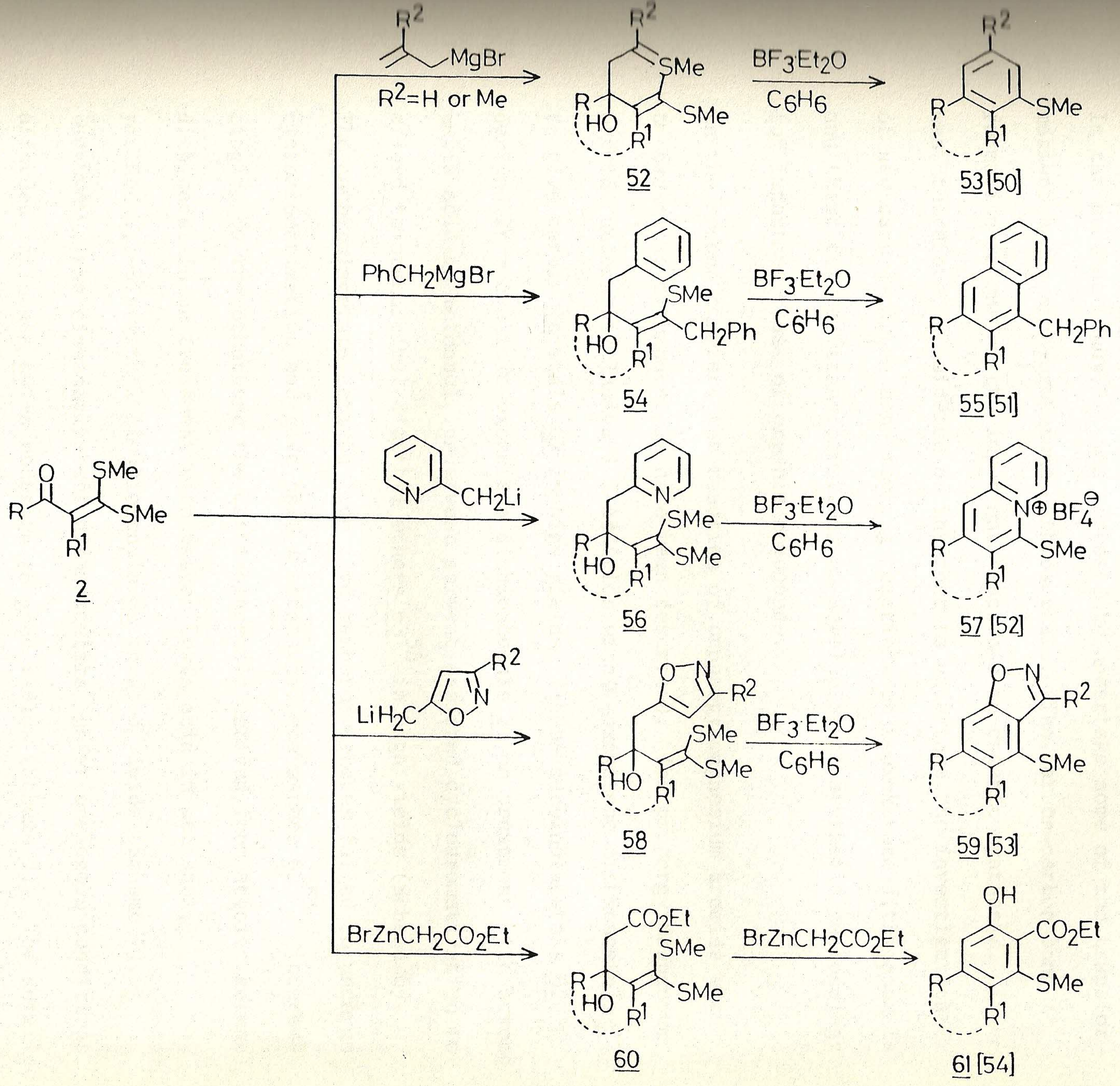
The Scheme 4 outlines the various transformations achieved from α-cinnamoyl and 5-aryl-2,4-pentadienoylketene dithioacetals. A general method for the synthesis of polyene esters 40[43] and γ,δ-unsaturated β-ketoester 42[45] have been developed. The corresponding cyclopentenones 41 and 43 are formed when the polyenes carry substituents at 2 and 4 positions. The styryl pyrimidines and pyridones 44, 45 and 46 were also synthesized[46,47]. It has also been shown that cinnamoylketene dithioacetals 39 undergo regioselective cyclopropanation and epoxidation at the styryl double bond. These intermediates were further exploited for the synthesis of pyrones 48[48] and cyclopentanones 50[49] and 51[49] respectively.

A new general method for aromatic annelation was developed by Singh, Ila and Junjappa[50]. The α-oxoketene dithioacetals 2 were shown to react with allylmagnesium bromide in an exclusive 1,2-fashion to give the corresponding allyl carbinolacetals 52 which underwent cycloaromatization on treatment with borontrifluoride etherate in benzene to afford annelated benzenoids[50]. The method is shown to be extremely versatile and found general applications for the synthesis of other benzenoids. Benzylmagnesium halides underwent the sequential 1,4- and 1,2-conjugate addition to yield the corresponding naphthoannelated products 55[51] under similar reaction conditions. Organolithium reagents such as 2-picolyllithium and 3-methyl-5-lithiomethylisoxazole also underwent regiospecific 1,2-addition and gave the corresponding quinolizium salts 57[52] and 1,2-benzisoxazoles 59[53]. The cycloaromatization



39
49 [49]
50 [49]
and
51 [49]
40 [43]
41 [44]
42 [45]
43 [45]
44 [46]
45 [47]
or
46 [47]
47 [48]
48 [48]
$(CH_3)_2\overset{O}{\overset{\|}{S}}^{\oplus}-CH_2^{\ominus}$
1. $NaBH_4$ / MeOH
2. $BF_3 \cdot Et_2O$ / MeOH
$BF_3 \cdot Et_2O$ / $HgCl_2$
MeOH
$HN=C(NH_2)_2$
NaOR
$CNCH_2CONH_2$
$NaOPr^i$
H_2O_2
NaOH
1. $BF_3 \cdot Et_2O$ / THF
2. AcOH / EtOH

Scheme 4

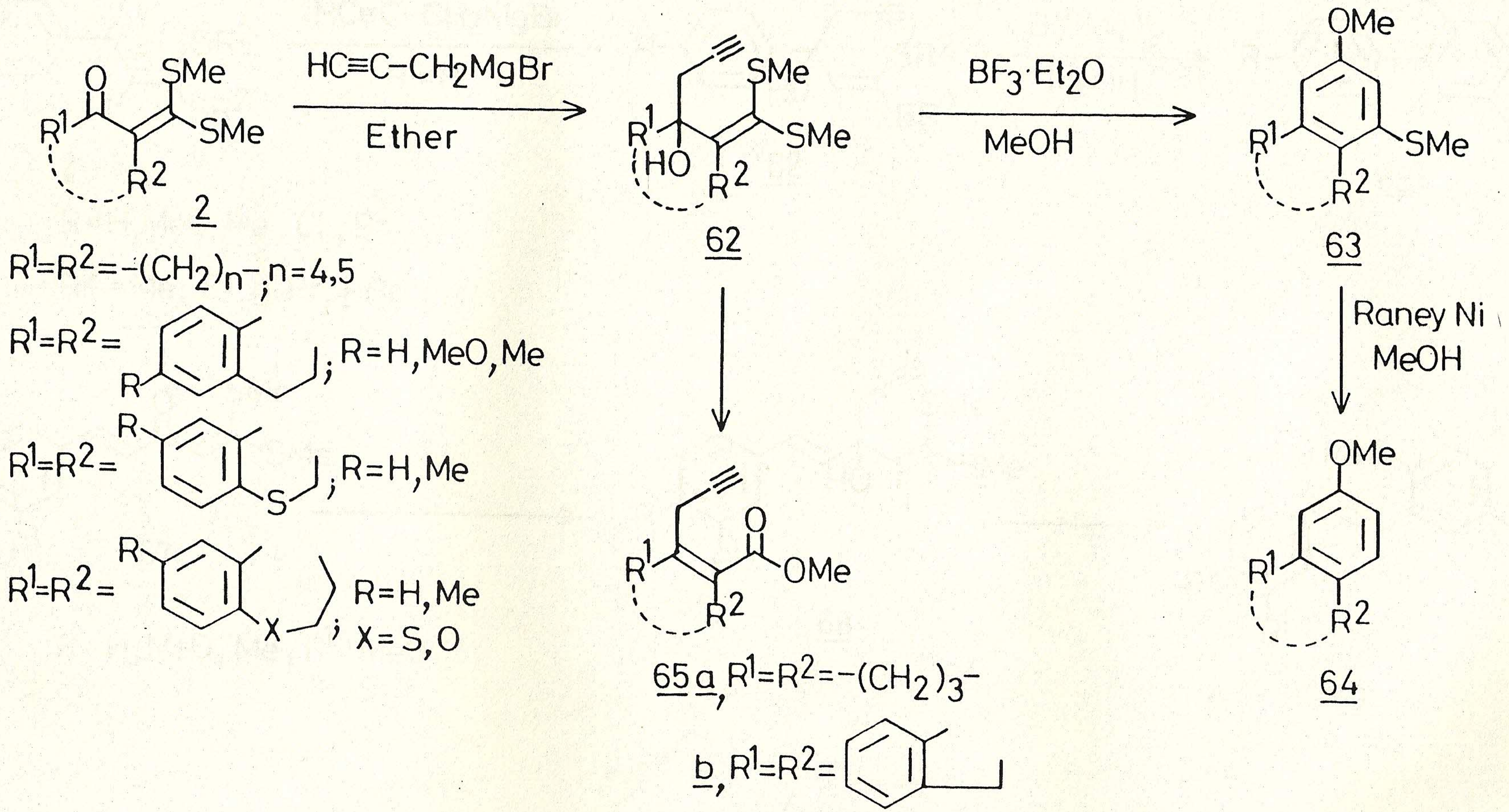

2
R²=H or Me
MgBr
PhCH₂MgBr
CH₂Li
LiH₂C
BrZnCH₂CO₂Et
BF₃·Et₂O
C₆H₆
52
53 [50]
54
55 [51]
56
57 [52]
58
59 [53]
60
61 [54]

Scheme 5

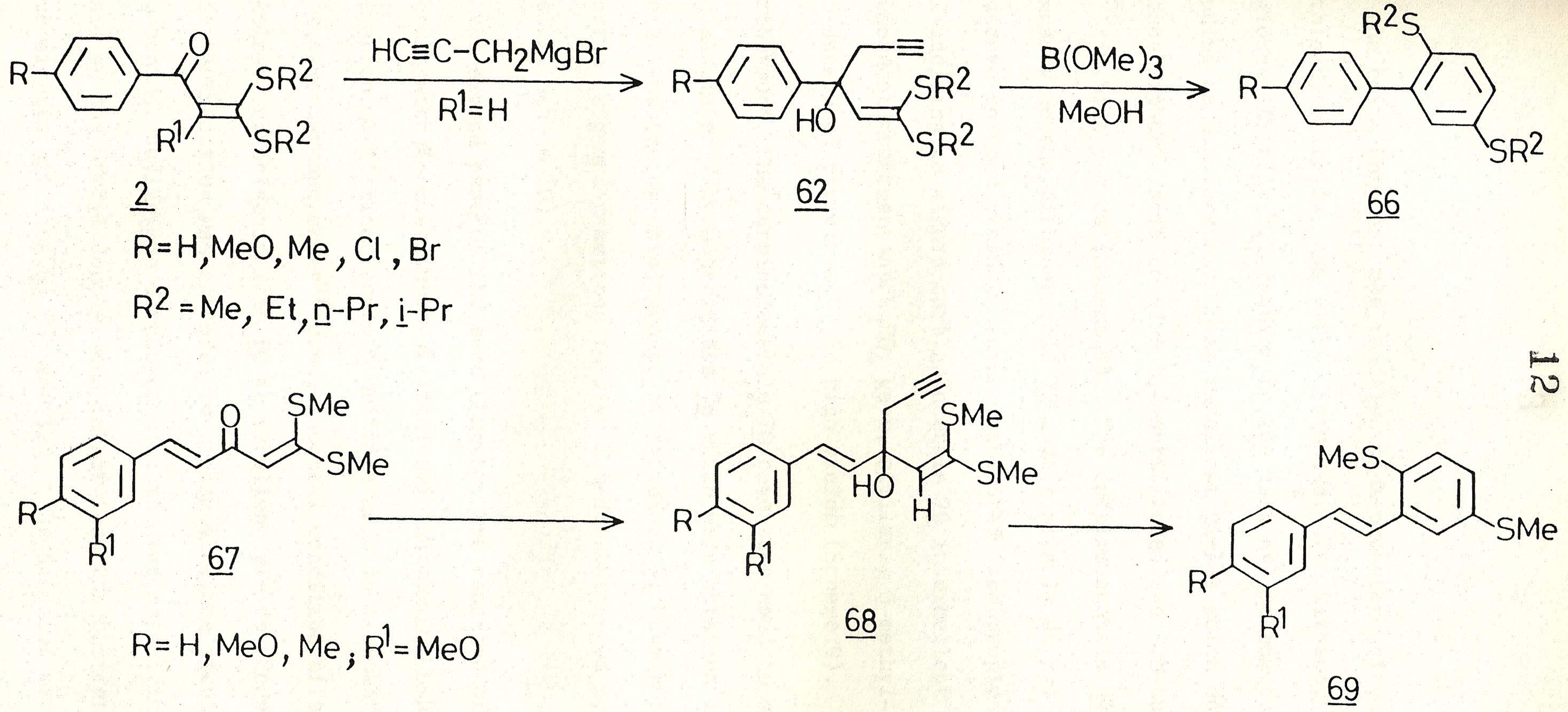
of α-oxoketene dithioacetals with Reformatsky reagent has ($BrZnCH_2CO_2Et$) also been reported to afford substituted and annelated salicylates 61[54] (Scheme 5).

In the present study, it was proposed to undertake some of the transformations based on α-oxoketene dithioacetals. The carbon-carbon bond formation is one of the important reactions in organic synthesis. It was, therefore, considered of interest to undertake the investigation of new carbon-carbon bond forming reactions on α-oxoketene dithioacetals and their further transformations to develop newer synthetic methodology for important class of organic compounds.

In the second chapter, the reaction of propargylmagnesium bromide with α-oxoketene dithioacetals have been described. The propargylmagnesium bromide undergo exclusive 1,2-addition with α-oxoketene dithioacetals 2 to give carbinolacetals 62 in high yields. These carbinolacetals 62, derived from cyclic α-oxoketene dithioacetals 2, on treatment with strong Lewis acid in methanol, underwent solvent assisted cycloaromatization to afford thioresorcinol dimethyl ethers 63[55] in high yields (Scheme 6). The carbinolacetals derived from five membered ketones failed to undergo cycloaromatization and gave only β-propargyl ene esters 65[55]. Interestingly, on the otherhand the carbinolacetals derived from acyclic ketene dithioacetals on treatment with weaker Lewis acid in methanol, yielded 2,5-bis(methylthio)biphenyls 66 in good yields (Scheme 7). Similarly, the cinnamoylketene dithioacetals, under analogous conditions, afforded stilbenes 69 in moderate to good yields (Scheme 7). The detailed mechanism of formation of biphenyls, stilbenes and thioresorcinol dimethylethers has also been discussed.


2
R¹=R²=-(CH₂)ₙ-; n=4,5
R¹=R²= ; R=H,MeO,Me
R¹=R²= ; R=H,Me
R¹=R²= ; R=H,Me; X=S,O
HC≡C-CH₂MgBr
Ether
62
BF₃·Et₂O
MeOH
63
Raney Ni
MeOH
64
65 a, R¹=R²=-(CH₂)₃-
b, R¹=R²=

Scheme 6

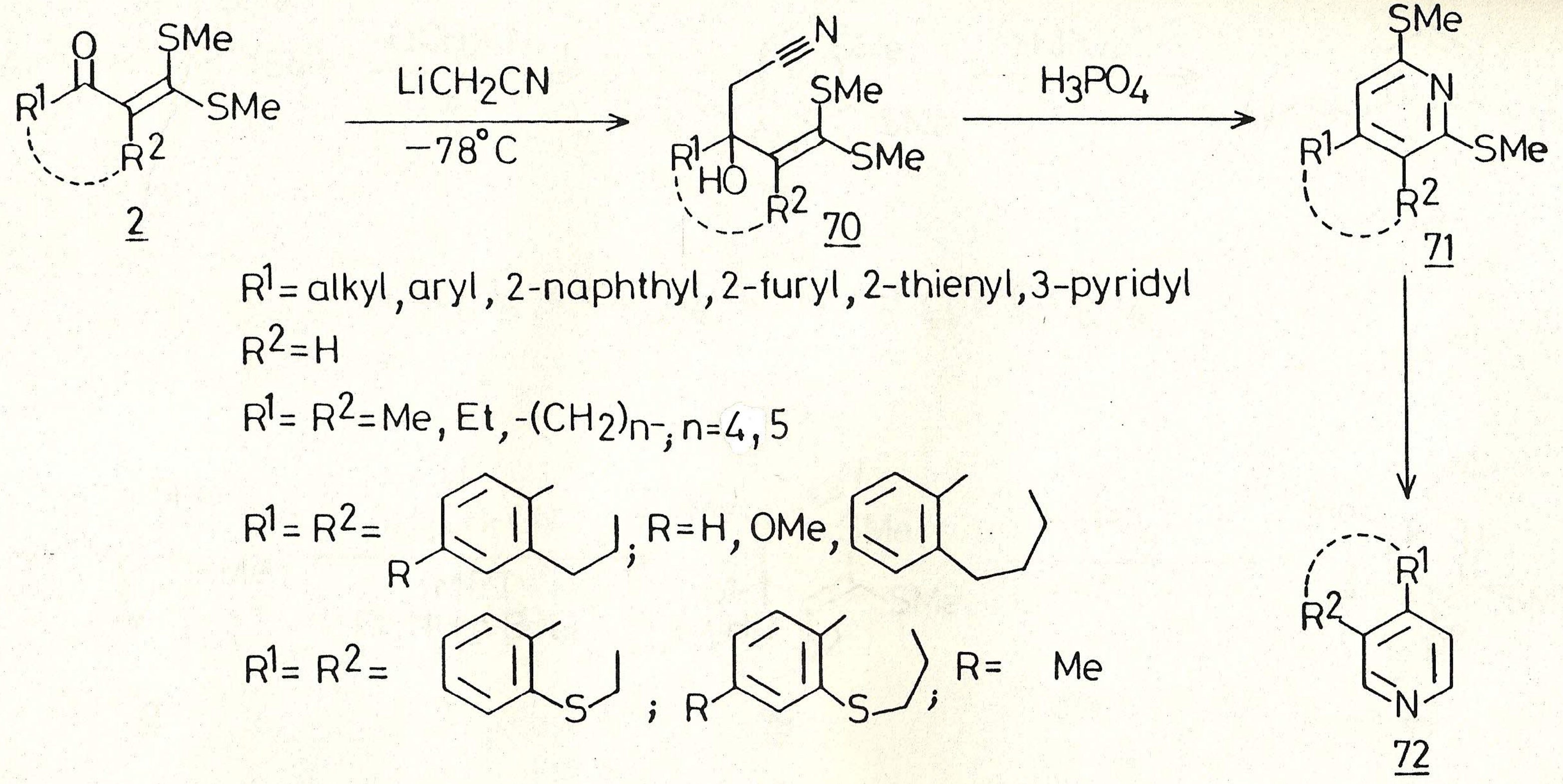

2
R=H,MeO,Me,Cl,Br
R2 =Me, Et,n-Pr,i-Pr
HC≡C-CH2MgBr
R1=H
62
B(OMe)3
MeOH
66
67
R=H,MeO,Me;R1=MeO
68
69

Scheme 7

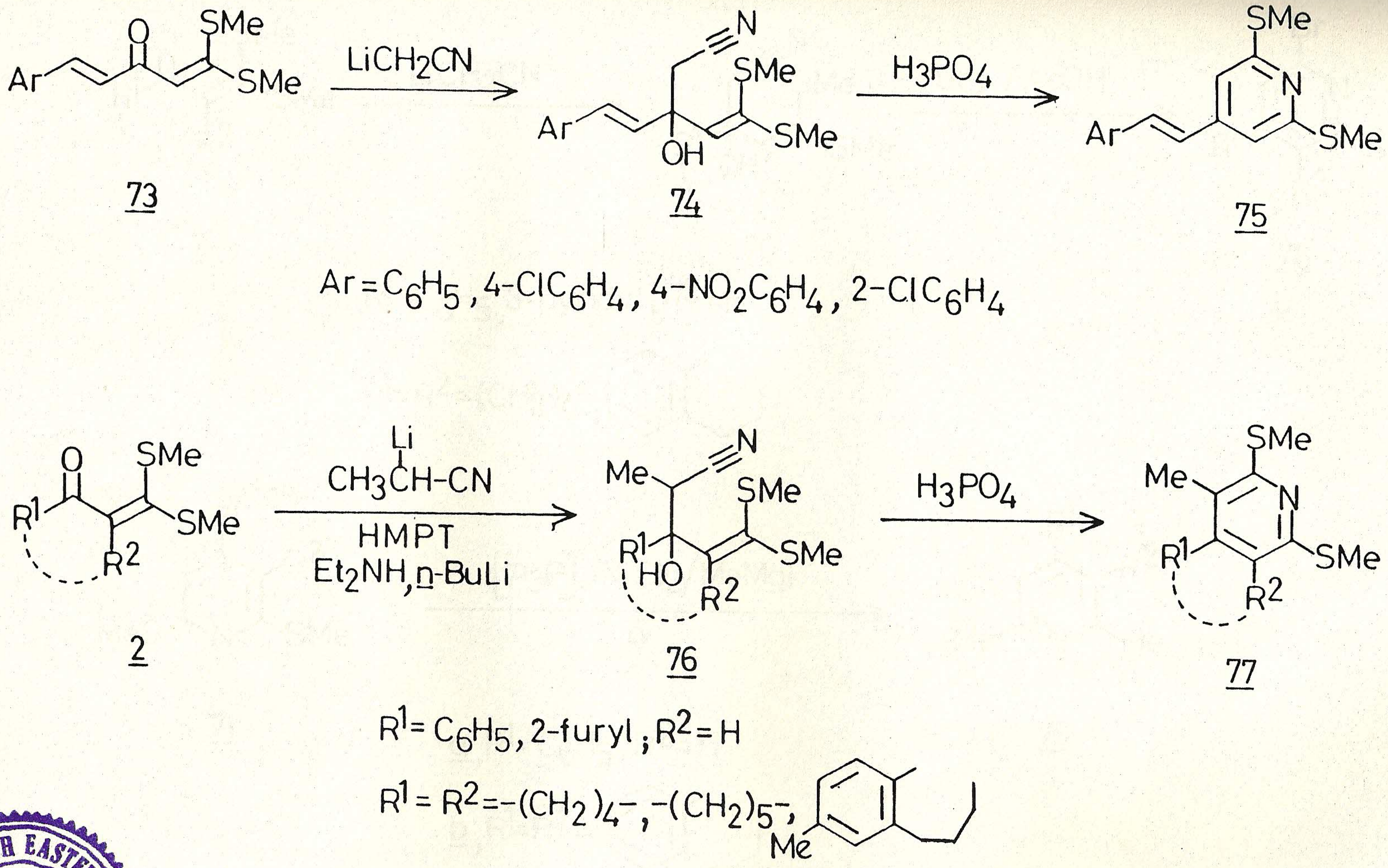
In the third Chapter, the reaction of α-oxoketene dithioacetals with lithioacetonitrile has been discussed. The lithioacetonitrile adds regiospecifically 1,2-fashion to the carbonyl carbon to give the corresponding carbinolacetals 70 in excellent yields which on treatment with orthophosphoric acid to give 3,4-substituted and 4,5-annelated pyridines 71[56] in high yields (Scheme 8). The carbinolacetals 74 derived from cinnamoylketene dithioacetals 73 gave similarly styryl pyridines 75 in moderate to good yields. Anion generated from propionitrile also underwent 1,2-addition to afford carbinolacetals 76 in excellent yields which on subsequent treatment with H_3PO_4 gave, similarly 3-methyl-4-substituted and 4,5-annelated pyridines 77 in high yields (Scheme 9).

Furthermore, the carbinolacetals 70 have been used to synthesize substituted and annelated 2-bromopyridines 78 which were obtained in excellent yields. The 2,6-bis(methylthio) groups of pyridines 71 have been replaced by Nickel induced Grignard reactions to give 2,6-disubstituted pyridines 79 in good yields (Scheme 10).

In the second part of the same Chapter, the reaction of α-oxoketene dithioacetals with β-substituted-β-lithioaminoacrylonitrile have been discussed. The anion, β-lithioaminocrotononitrile adds to α-oxoketene dithioacetals 2 in 1,4-manner and under the experimental condition affords substituted and annelated nicotinonitriles 80 in excellent yields (Scheme 11). Similarly, when the reaction was extended to cinnamoylketene dithioacetals and 5-aryl-2,4-pentadienoylketene dithioacetals, the regiospecific 1,4-addition took place on the styryl double bond rather than the bis(methylthio) carbon to give nicotinonitriles 81 (Scheme 12). The detailed mechanism of formation of these substituted and annelated nicotinonitriles have been discussed in


2
LiCH2CN
−78°C
70
H3PO4
71
72
SMe
R1
R2
HO
N
R1= alkyl, aryl, 2-naphthyl, 2-furyl, 2-thienyl, 3-pyridyl
R2=H
R1= R2=Me, Et, -(CH2)n-; n=4, 5
R1= R2= ; R=H, OMe,
R1= R2= ; R ; R= Me

Scheme 8



Ar = C_6H_5, 4-ClC_6H_4, 4-$NO_2C_6H_4$, 2-ClC_6H_4

$R^1 = C_6H_5$, 2-furyl ; $R^2 = H$

$R^1 = R^2 = -(CH_2)_4-, -(CH_2)_5-,$

Scheme 9

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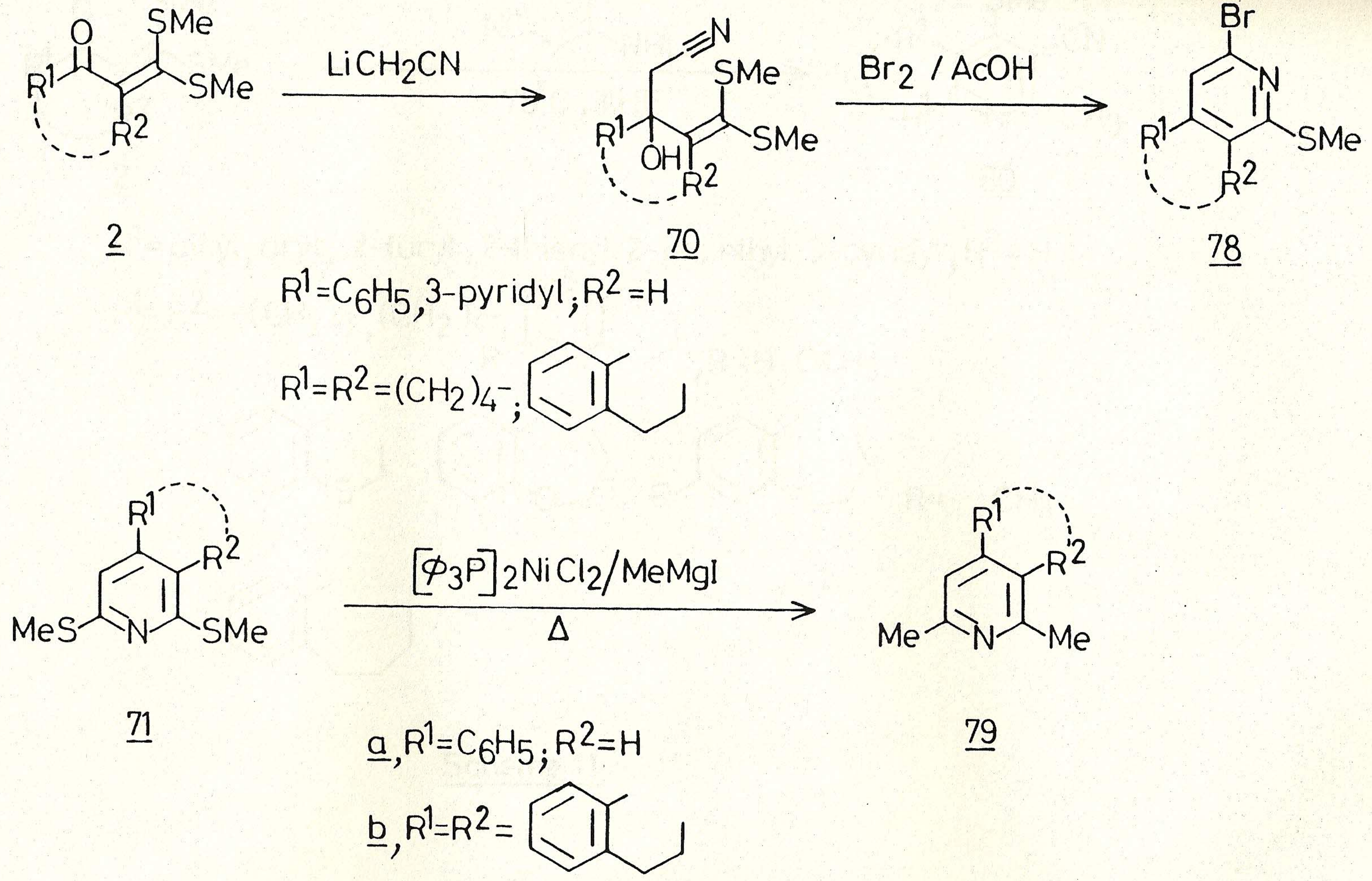
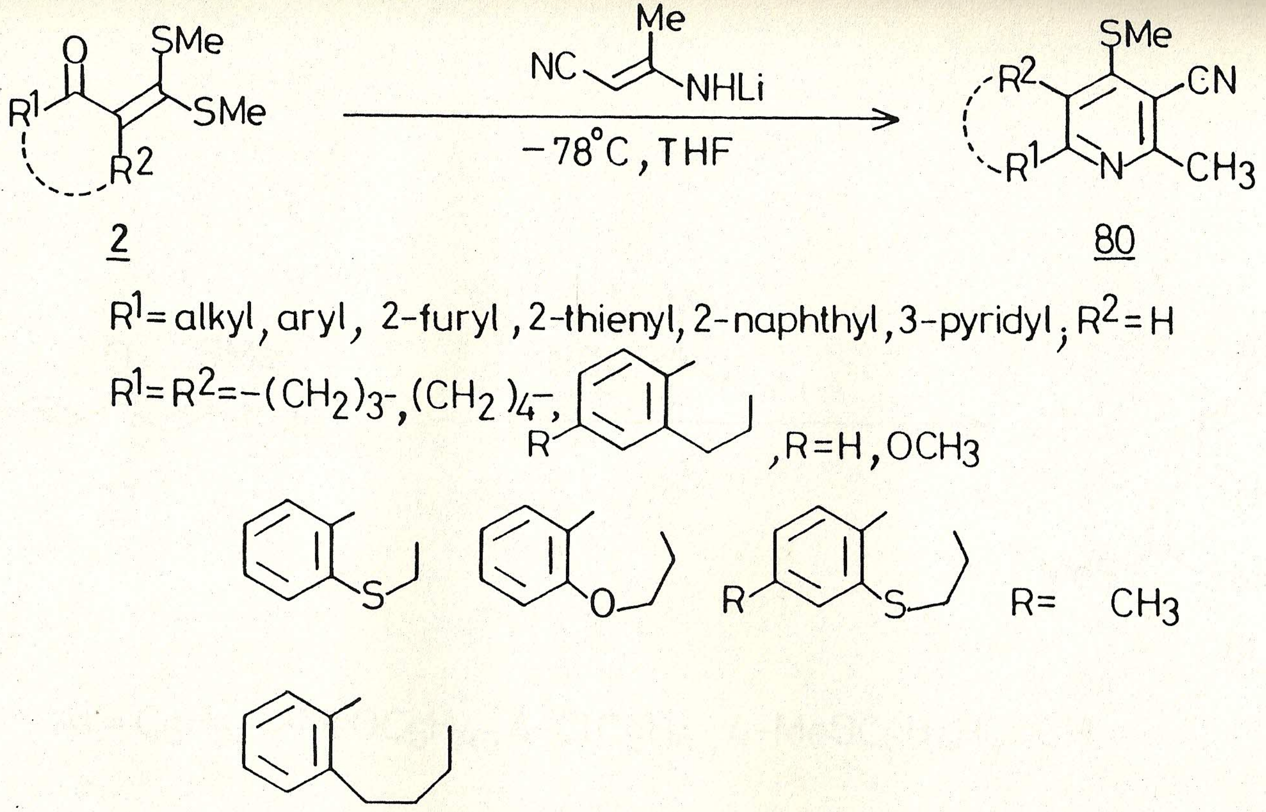

LiCH2CN
Br2 / AcOH
[Φ3P]2NiCl2/MeMgI
Δ
SMe
O
R1
R2
OH
N
Br
Me
MeS
2
70
78
71
79
R1=C6H5, 3-pyridyl; R2=H
R1=R2=(CH2)4–;
a, R1=C6H5; R2=H
b, R1=R2=

Scheme 10



2

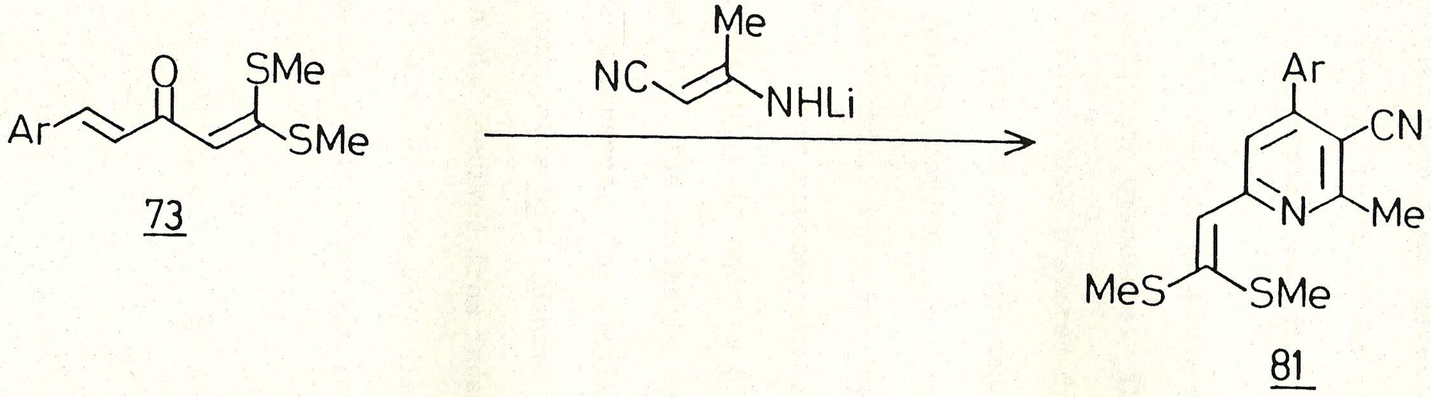
80

R^1= alkyl, aryl, 2-furyl, 2-thienyl, 2-naphthyl, 3-pyridyl; R^2= H

R^1= R^2= $-(CH_2)_3-$, $(CH_2)_4-$, , R = H, OCH_3

R = CH_3

Scheme 11

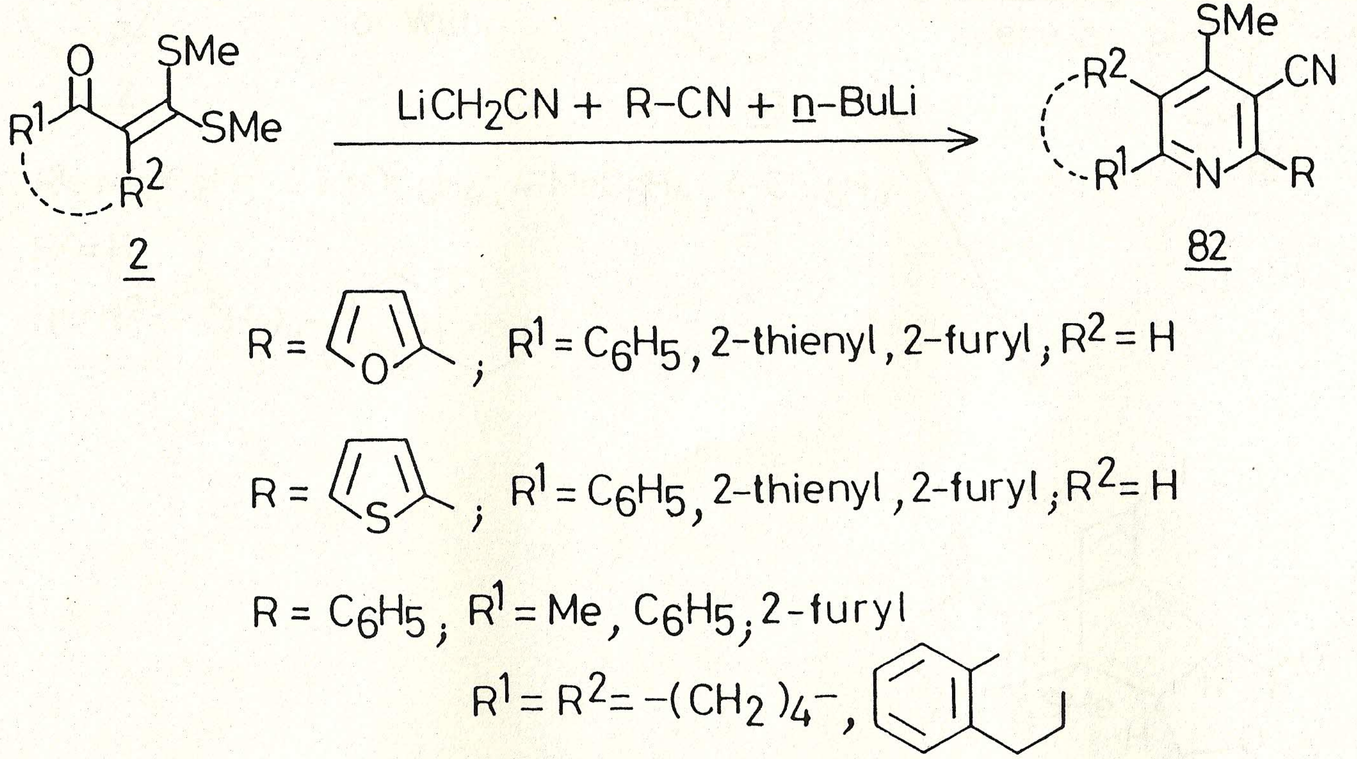


Ar = C_6H_5, 4-$MeOC_6H_4$, 4-ClC_6H_4, 4-$MeOC_6H_4HC{=}CH$

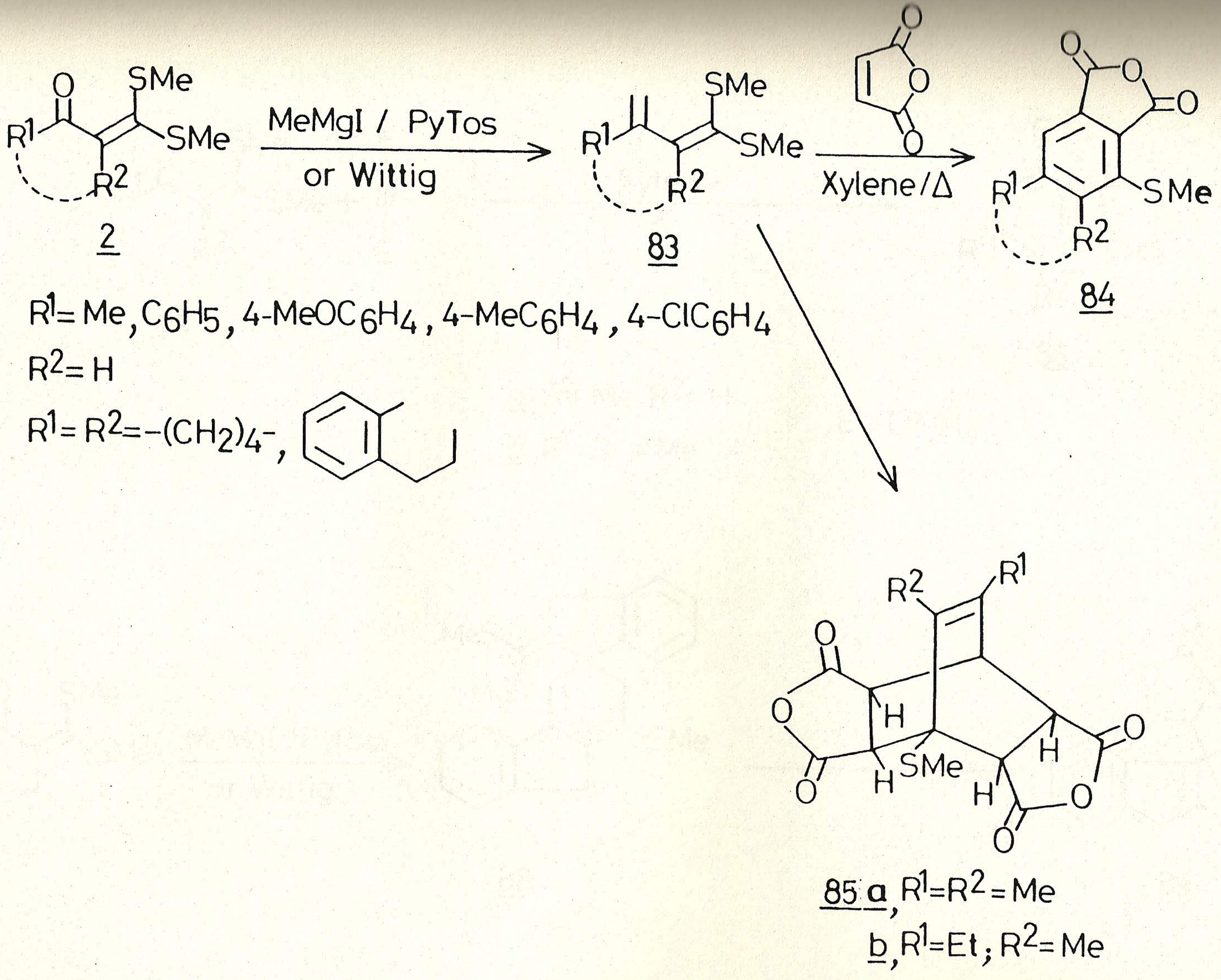
Scheme 12

this Chapter. β-Substituted β-lithioaminoacrylonitrile anions have also been generated and added to the α-oxoketene dithioacetals 2 which under the analogous experimental condition, gave 2,6-disubstituted and 2,3-annelated nicotinonitriles 82 in excellent yields (Scheme 13). The reduction studies of these product pyridines have also been described.

In the fourth Chapter, the studies on Diels-Alder cycloaddition of vinylketene dithioacetals have been discussed. The diene vinylketene dithioacetals 83 have been conveniently prepared from the corresponding α-oxoketene dithioacetals 2, and are shown to react with doubly activated dienophiles, such as maleic anhydride to give cycloadducts phthalic anhydrides 84[57] in good yields. When vinylketene dithioacetals with $R^1=R^2=Me$ and $R^1=Et, R^2=Me$, were reacted with maleic anhydride under analogous conditions, the bicyclic adducts 85a and 85b were obtained in high yields (Scheme 14). The mechanism of formation of these bicyclic adducts have also been discussed. The vinylketene dithioacetals with DMAD afforded substituted phthalates 86[57] (Scheme 15). Attempted preparation of vinylketene dithioacetal derived from indanone 87 by either of the methods (dehydration or Wittig) gave only dimeric adduct 88. Adduct 89 was also obtained when the crude diene was reacted with maleic anhydride (Scheme 15).


2
LiCH2CN + R–CN + n-BuLi
82
R = ; R1 = C6H5, 2-thienyl, 2-furyl; R2 = H
R = ; R1 = C6H5, 2-thienyl, 2-furyl; R2 = H
R = C6H5; R1 = Me, C6H5; 2-furyl
R1 = R2 = –(CH2)4–,

Scheme 13



2

83

84

R^1= Me, C_6H_5, 4-$MeOC_6H_4$, 4-MeC_6H_4, 4-ClC_6H_4

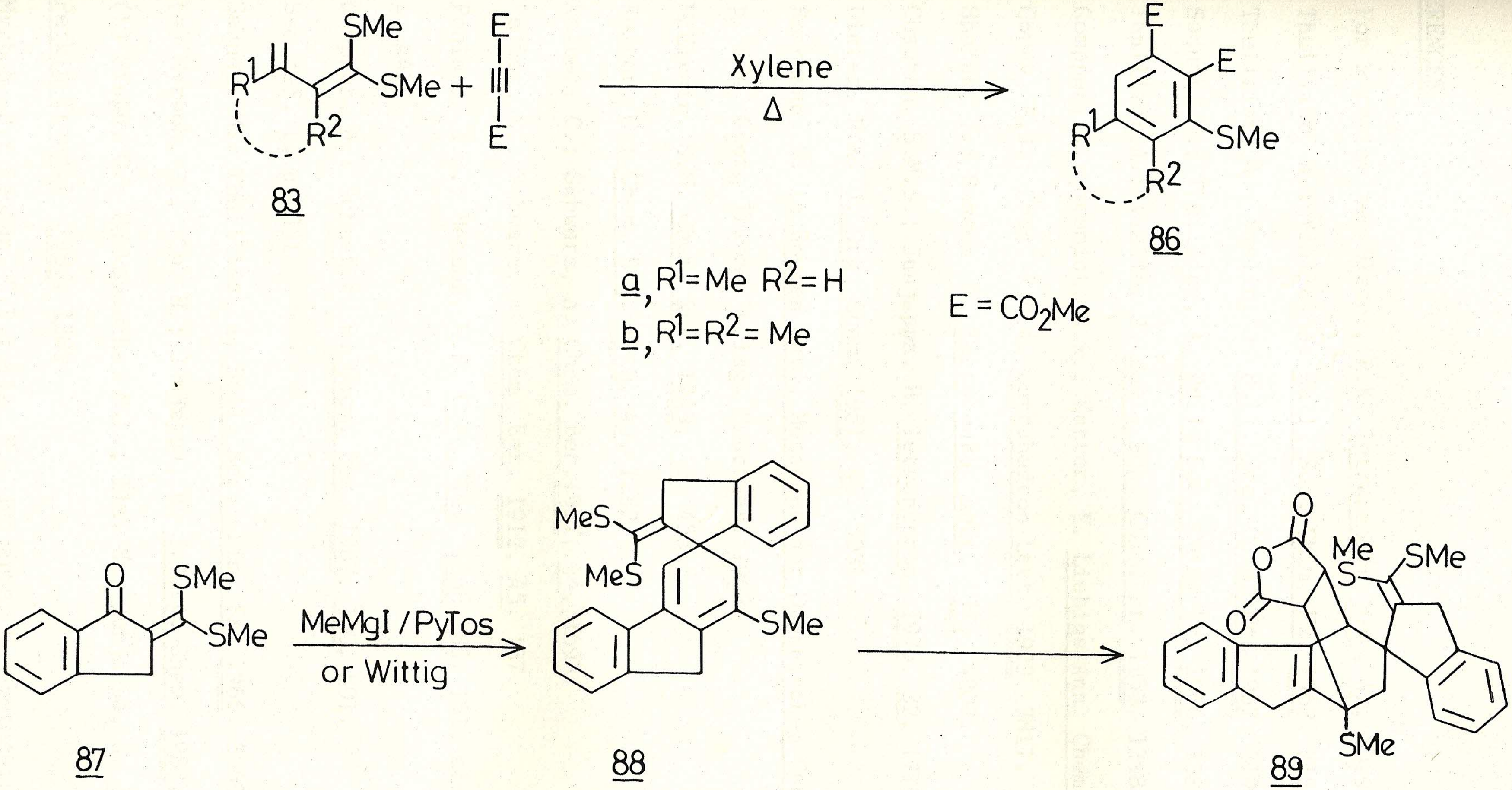
R^2= H

R^1= R^2= –$(CH_2)_4$–,

85 a, R^1=R^2= Me

b, R^1=Et; R^2= Me

Scheme 14



83 86

a, R^1=Me R^2=H

b, R^1=R^2= Me

E = CO_2Me

87 88 89

Scheme 15

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