Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 7251–7271

TETRAHEDRON

Tetrahedron report number 649

The thio-Claisen rearrangement 1980–2001

Krishna C. Majumdar,* Subhojit Ghosh and Manish Ghosh

Department of Chemistry, University of Kalyani, Kalyani, West Bengal 741 235, India

Received 24 June 2003

Contents

1. Introduction

The first appearance of the thio-Claisen rearrangement (TCR) in the literature[1] occurred in 1962. The TCR is the sulfur analogue of the simple Claisen rearrangement.[2–6] Classically, it is a [3,3] sigmatropic rearrangement[7] in the allyl vinyl sulfides leading to a homoallyl thiocarbonyl unit. Since its first appearance in literature, the mechanistic aspects of the TCR, especially the mechanistic relationship to the oxy-Claisen process, have received[8–11] considerable attention.

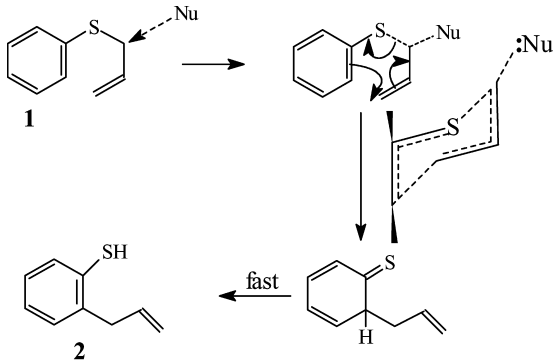
2. Mechanistic aspects

The role of a wide variety of both neutral and anionic nucleophiles[12] in the concerted [3,3] sigmatropic rearrangement of phenyl allyl sulfides **1** leading to 2-allylthiophenols **2** has been thoroughly investigated. Scheme 1 illustrates the proposed reaction course and the geometrical details of the transition state involved.

Overman et al.[13] have advanced a mechanistic proposal for the cyclisation-induced catalysis of the [3,3] sigmatropic rearrangement in the sulfur series involving the following pathway (Scheme 2).

According to these workers, the catalyst forms a σ-bond to the β-(side chain)-carbon, leading to an intermediate **3** closely resembling the transition state. Kwart et al.[14] have investigated the corresponding secondary deuterium isotope effect and the effects of substitution on the reaction rates.

Vialle et al.[15] have suggested a diradicaloid transition state along with an aromatic transition state for the thio-Claisen process of the allyl vinyl sulfides **4** to form **5**. In the oxygen series, the activation enthalpy of the corresponding diradicaloid transition state has been estimated[16] to be 7 kcal/mol higher than the aromatic transition state. The



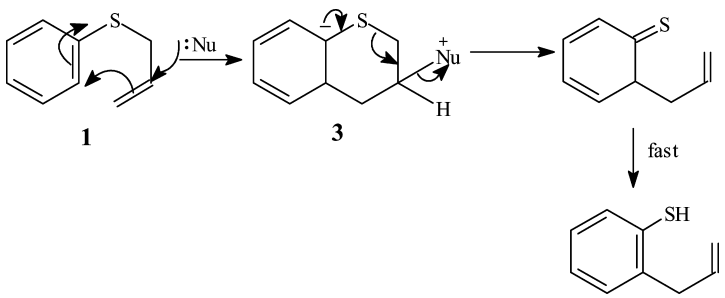
Scheme 1.

Keywords: thio-Claisen rearrangement; diradicaloid transition state; aminothioacetal; [3,3]sigmatropic rearrangement; sulfur heterocycles.

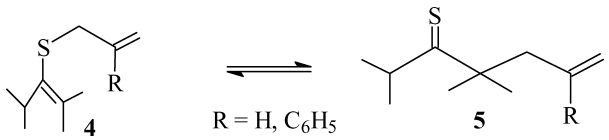
Abbreviations: TCR, thio-Claisen rearrangement; DBU, diazabicyclo[5,4,0]undec-7-ene; DIPEA, *N*,*N*-diisopropylethylamine; $Ni(COD)_2$, dicyclooctadienyl nickel; MEM, methoxyethoxymethyl; TBDMS, *t*-butyldimethylsilyl; *N*,*N*-DEA, *N*,*N*-diethylaniline.

* Corresponding author. Tel.: +91-33-2582-7521; fax: +91-33-2582-8282; e-mail: kcm@klyuniv.ernet.in

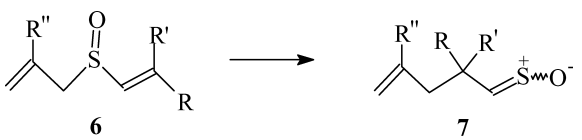
0040–4020/$ - see front matter
doi:10.1016/S0040-4020(03)01023-8



Scheme 2.



Scheme 3.

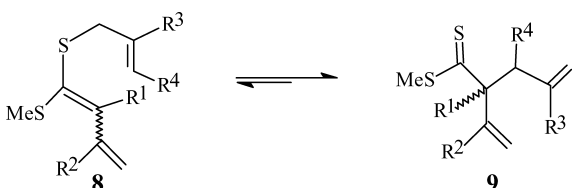


R	R'	R"	*E*:*Z* of sulfine **7**
H	H	H	5:95
CH_2Cl	H	H	2:98
Me	H	H	2:98
C_6H_5	H	H	2:98
H	H	Me	33:66
Me	Me	H	70:30
—$(CH_2)_5$—		H	83:17
2-adamantylidine		H	65:35

Scheme 4.

sulfur atom is, however, known to exert[17] an important stabilising influence on the α-carbon radical of the diradicaloid transition state (Scheme 3).

The introduction of a radical-stabilising group (e.g. R=Ph) stabilises the diradicaloid transition state by 4–8 kcal/mol[16,18] and the possible involvement of this transition state should not be precluded. The kinetics of the TCR of a

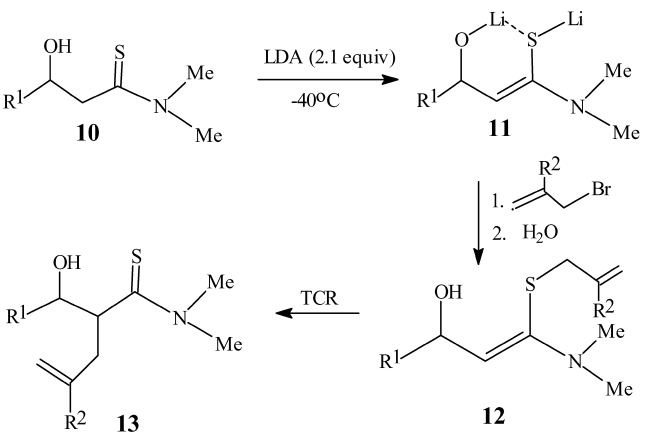


R^1	R^2	R^3	R^4
H	H	H	H
H	H	Me	H
H	H	H	Me
Me	H	H	H
Me	H	Me	H
Me	H	H	Me
H	Me	H	H
H	Me	Me	H
H	Me	H	Me

Scheme 5.

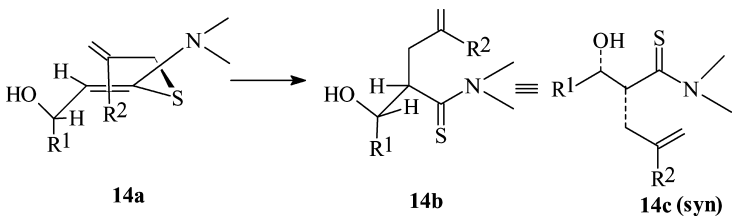
number of 5-substituted allyl 2-thienyl sulfides[19] demonstrate that a decrease in the aromatic character of the pericyclic transition state diminishes the reactivity of the sulfides.

The kinetics and energetics of the TCR[20] of 2-butenyl 2-benzofuryl sulfide, cyclopenten-2-yl 2-benzofuryl sulfide, 2-butenyl 2-benzothienyl sulfide and cyclopenten-2-yl 2-benzothienyl sulfide have been studied. The effect of the substrate structure, the polarity of the solvent and the temperature on the course of the reaction has also been investigated. The 1,3-thioallyl rearrangement of 1-methylallyl 3-methyl-2-benzothienyl sulfide is shown to compete effectively with the corresponding thio-Claisen process. The kinetic data for the formation of uncondensed heterocycles[21] through the rearrangement of allyl hetaryl sulfides, with an allyl segment being a part of a heteroaromatic ring, reflect that the incorporation of the vinyl or allyl unit in the heteroaromatic ring of the sulfide gradually represses

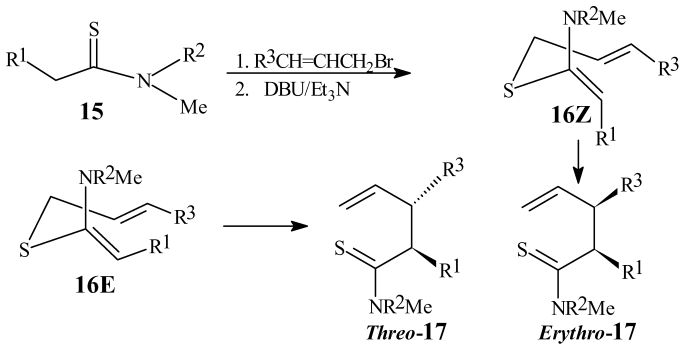


R^1	R^2	syn:anti (**13**)
Me	H	80:20
Et	H	85:15
Pr^i	H	93:7
Bu^t	H	>98:2
C_6H_5	H	80:20
$C_6H_5CH_2$	H	90:10
C_6H_5CHMe	H	> 95:5
Me	Me	80:20
Et	Me	85:15
Pr^i	Me	85:15
Bu^t	Me	> 98:2
$C_6H_5CH_2$	Me	95:5

Scheme 6.



Scheme 7.



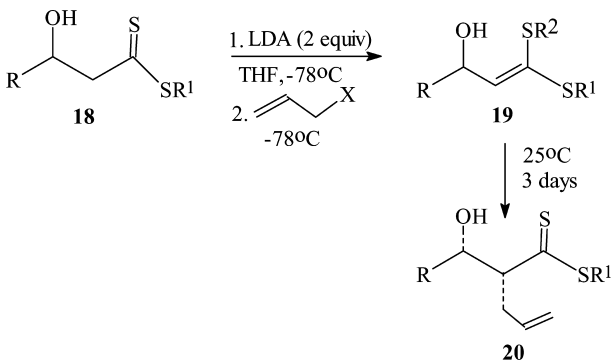
R^1	R^2	R^3	Base	Conditions	*Erythro*-**17** : *Threo*-**17**
Me	Me	Me	DBU	r.t, 6 h	24:1
Me	Me	Me	DBU	70°C, 4 h	6.7:1
Me	Me	C_6H_5	DBU	r.t, 6 h	13:1
Pr^i	Me	Me	DBU	85°C, 5 h	1.2:1
N,N-dimethylthio crotonamide		Me	DBU	r.t, 9 h	24:1
N,N-dimethylthio crotonamide		Me	DBU	85°C, 4 h	2.9:1
C_6H_5	Me	Me	DBU	70°C, 4 h	4:1
C_6H_5	Me	Me	Et_3N	r.t, 43 h	13:1
—$(CH_2)_3$—		Me	Et_3N	85°C, 2 h	1:9
—$(CH_2)_3$—		C_6H_5	DBU	85°C, 4 h	1:1.1
—$(CH_2)_3$—		C_6H_5	Et_3N	85°C, 4 h	1:99
—$(CH_2)_4$—		C_6H_5	Et_3N	83°C, 4 h	1:99

Scheme 8.

the rearrangement with an increase in aromatic character of the hetero-ring.

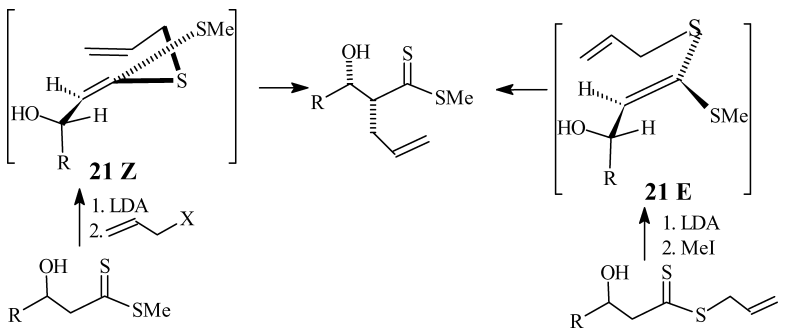
The TCR of the allyl vinyl sulfoxides **6** giving rise to sulfine **7** is, however, found[22] to be much faster compared to that of the allyl vinyl sulfides. The activation enthalpy for this sulfoxide TCR ($H^{\#}$=19.32±0.5 kcal/mol; $S^{\#}$=−4.30±1.60 cal/mol) has been estimated to be lower than that for the Claisen rearrangement of allyl vinyl ether ($H^{\#}$=25.40 kcal/mol; $S^{\#}$=−15.9 cal/mol) (Scheme 4).[23]

This low $H^{\#}$ value for the sulfoxide thio-Claisen reaction is possibly due to the low C–S(O) bond strength compared to the C–S or C–O bond strengths. The negatively charged oxygen in the sulfoxides may render the pericyclic process analogous to the anion- or alkoxide-assisted Cope or Claisen rearrangements which are more facile than their non-assisted counterparts. Again, the thio-Claisen process suffers from a loss of conjugation between sulfur lone pairs and the 1-alkenyl segment in the non-planar, chair-like transition state, while there is no such loss of conjugation in the sulfoxide TCR.

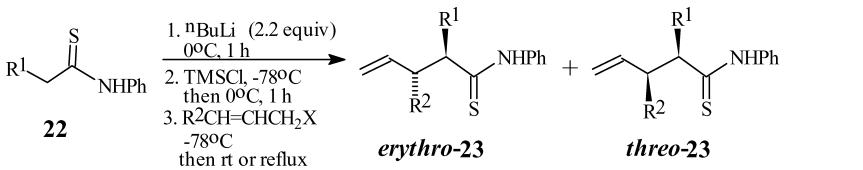


R	R^1	R^2	*syn:anti* (**20**)
Me	Me	allyl	9:1
Et	Me	allyl	13:1
Pr	Me	allyl	16:1
Pr^i	Me	allyl	24:1
Bu^t	Me	allyl	> 24:1
C_6H_5	Me	allyl	6:1
$C_6H_5CH_2$	Me	allyl	24 : 1

Scheme 9.

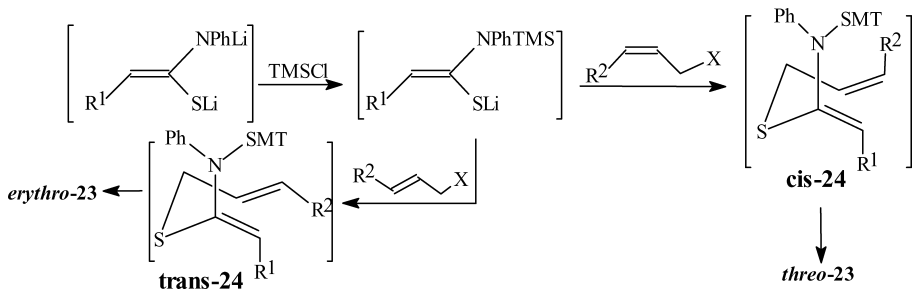


Scheme 10.

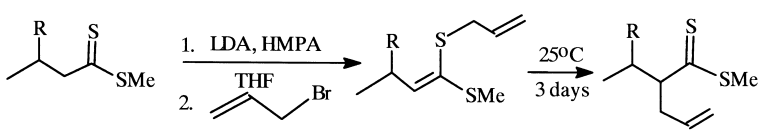


thioamide **22**		allylating agent		*erythro* **23** : *threo* **23**
R^1	stereochemistry	R^2	X	
Me	trans	Me	OTs	99 :1
Me	cis	Me	OTs	1 : 99
Me	trans	C_6H_5	Br	99 : 1
Me	trans	CH_2SiOMe_3	Cl	10 : 90
Me	cis	CH_2SiOMe_3	Cl	91 : 9
C_6H_5	trans	Me	OTs	99 : 1
C_6H_5	cis	Me	OTs	1 : 99
C_6H_5	trans	C_6H_5	Br	99 : 1

Scheme 11.



Scheme 12.

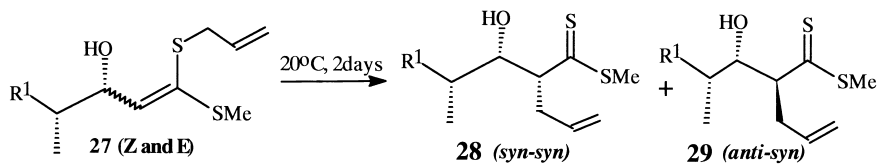


R	***syn*/*anti***
Pr^i	77:23
Ph	82:18
Bu^t	95:5

Scheme 13.

Introduction of additional unsaturation[15,24] in the sulfides causes a decrease in activation enthalpy for the thio-Claisen process as compared to the oxygen analogues. The reversibility of the TCR has been investigated by Vialle et al.,[15,24] who reported that γ-unsaturated thioketones equilibrate with allyl vinyl sulfides. Reversibility in the TCR of ketene dithioacetals **8** has also been investigated (Scheme 5).[25]

The position of equilibrium between **8** and **9** has been shown

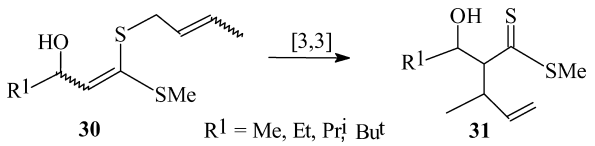


27 (Z and E) 28 (syn-syn) 29 (anti-syn)

R^1	dithioacetal **27**	*syn-syn/anti-syn*
Bu^t	Z	85:15
Bu^t	E	94:6
C_6H_5	Z	99:1
C_6H_5	E	99:1
cyclohexyl	Z	89:11
cyclohexyl	E	98:2

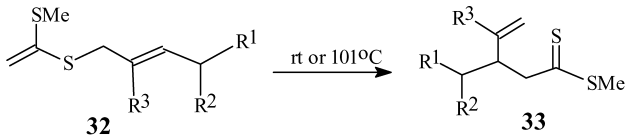
Scheme 14.

to be a function of the substitution pattern of the carbon chain. A greater steric demand around the newly constructed C–C bond shifts the equilibrium more towards the left and it is therefore clear that the Claisen rearrangement, like other [3,3] sigmatropic processes, follows thermodynamic control. This effect is not encountered in the oxygen series, presumably due to a large stability difference between the reactant and product. In the sulfur analogues, however, the similar formation enthalpies of the reactant and product make the reversibility more distinct.

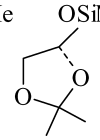


30 R^1 = Me, Et, Pr^i, Bu^t **31**

Scheme 15.



32 **33**

R^1	R^2	R^3	C=C configuration	*syn* : *anti* (33)
Me	C_6H_5	H	E	70:30
Me	Bu^t	H	E	75:25
Me	OMEM	H	E	54:46
Me	$OCH_2C_6H_5$	H	E	53:47
Me	$OSiMe_2Bu^t$	H	E	66:34
		H	E	65:35
Me	$OCH_2C_6H_5$	Me	E/Z = 50:50	61:39
Me	$OCH_2C_6H_5$	Me	E	61:39
Me	$OCH_2C_6H_5$	Me	Z	60:40

Scheme 16.

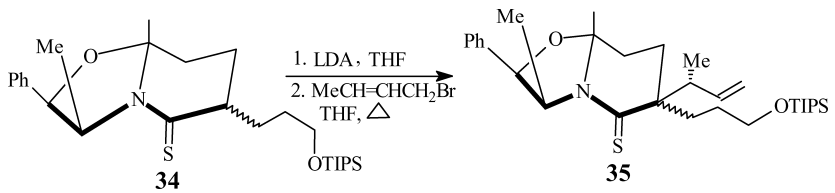
3. Stereoselectivity

The stereospecificity[26–28] of the TCR has been investigated quite thoroughly and this finds use in diastereoselective syntheses. The β-hydroxythioamides **10** undergo di-deprotonation with LDA at −40°C. Allylation of the dilitho species **11** with various allyl bromides affords the α-allyl-β-hydroxythioamides **13** through a TCR of **12**, with preponderant *syn* diastereoselectivity ranging from 80:20 to 98:2, through the TCR of the *S*-allylic ketene aminothioacetals (Scheme 6).[29]

The predominance of the *syn* diastereomer has been explained in terms of the model **14a–c** which places H in the 'inside position', R^1 in the 'outside position' and the OH group perpendicular to the ketene plane. The new C–C bond is formed on the more electron-rich face of the ketene which is *syn* to the hydroxyl functionality (Scheme 7).

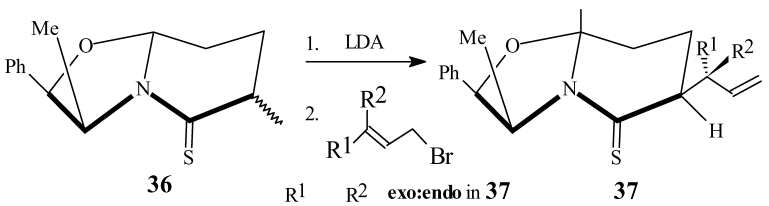
Allylation of the thioamides **15** in the presence of DBU or Et_3N affords[30] a diastereomeric mixture of *erythro*- and *threo*-α-allylthioamides **17** through the TCR of the *S*-allylic ketene aminoacetals **16**. Stereoselective generation of the *Z*-ketene *S*,*N*-acetals gives rise to a preponderance of the *erythro*-diastereomer (Scheme 8).

The steric bulk of the R^1 group seems to influence the rate of rearrangement. The bulk of the R^3 group, however, has not been found to have an effect on the course of the rearrangement.



34 **35**

Scheme 17.

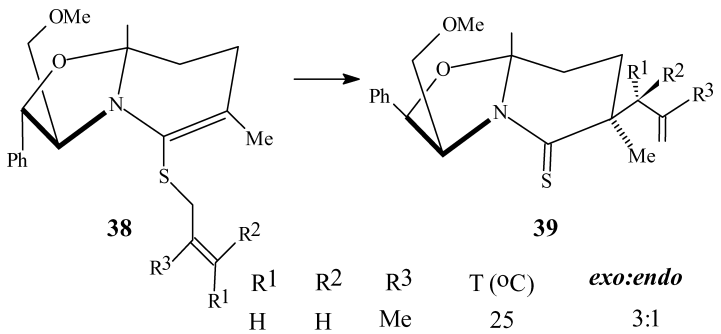


36

R^1	R^2	exo:endo in **37**
H	H	1.7:1
Me	H	1.8:1
Me	Me	15:1

37

Scheme 18.



38 **39**

R^1	R^2	R^3	T (°C)	*exo:endo*
H	H	Me	25	3:1
Me	H	H	25	91:1
Ph	H	H	140	> 99:1
Me	Me	H	140	> 99:1

Scheme 19.

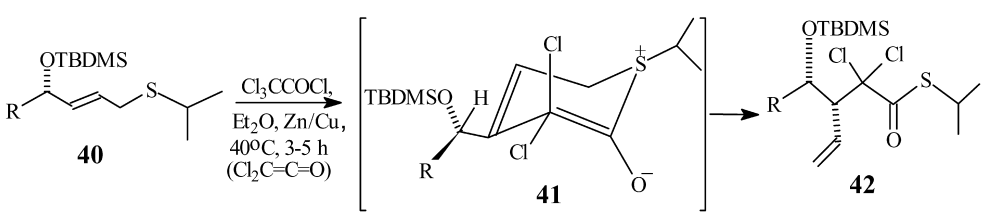
Deprotonation of the β-hydroxydithioesters **18** with two equivalents of LDA, followed by allylation at −78°C, furnishes the stereochemically pure *Z*-*S*-allyl-α-hydroxyketene dithioacetals[31] **19**. At room temperature, **19** undergoes a TCR leading to a mixture of the *syn* and *anti* diastereomers of the α-allyl-β-hydroxydithioesters **20**, with a *syn*/*anti* ratio in the range 6:1 to 24:1 (Scheme 9).

The *syn* diastereoselectivity of this rearrangement may arise from a steric or an electronic effect or both. The formation of a bond between the allylic fragment and the ketene carbon takes place *anti* to the R group, the A-strain of which is greater than that of the OH group. In the transition state **21** the OH group occupies the 'outside position' almost in the ketene plane due to steric repulsion and stabilisation derived from a through-space interaction between the oxygen lone pair and the ketene dithioacetal π-system. This *syn* diastereoselectivity is shown to be independent of the ketene dithioacetal geometry by converting the *E*-isomer of **19** (R^1=allyl; R^2=Me) into a 10:1 *syn*–*anti* mixture of **20** (Scheme 10).

A highly diastereoselective α-allylation of secondary and tertiary thioamides is accomplished[32] via the TCR. The secondary thioamides **22**, on allylation, give a diastereomeric mixture of the *threo*- and *erythro*-α-allylated thioamides **23** (Scheme 11).

The *Z*-isomer of the dianion of **22** should give *erythro*-**23** on reaction with the allylating agent in its *E*-form and reaction with the allylating agent in the *Z*-form should produce *threo*-**23** through the transition state **24** in the *trans* and *cis* forms, respectively (Scheme 12).

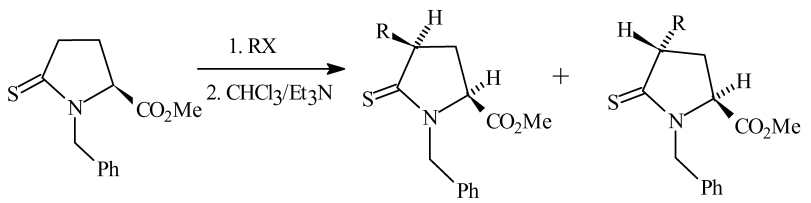
A correlation between the diastereoselectivities in the products and the structures of the allylating agents reveals the almost exclusive formation of the *Z*-form of the secondary thioamide dianion and the tertiary thioamide



40 **41** **42**

R = Me, Pr^i, C_2H_4OTBDMS

Scheme 20.



44. R = allyl **45**. R = allenyl **46**. R = methallyl, X = Br

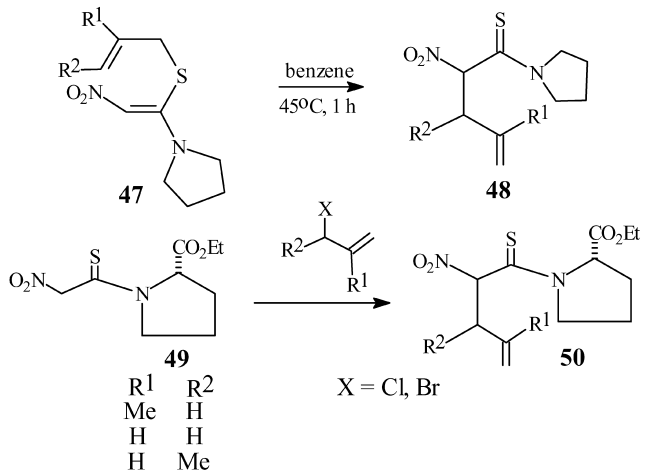
Scheme 21.

anion. The *erythro–threo* ratio therefore depends on the geometry of the allylating agents and the steric bulk of the R^2 group.

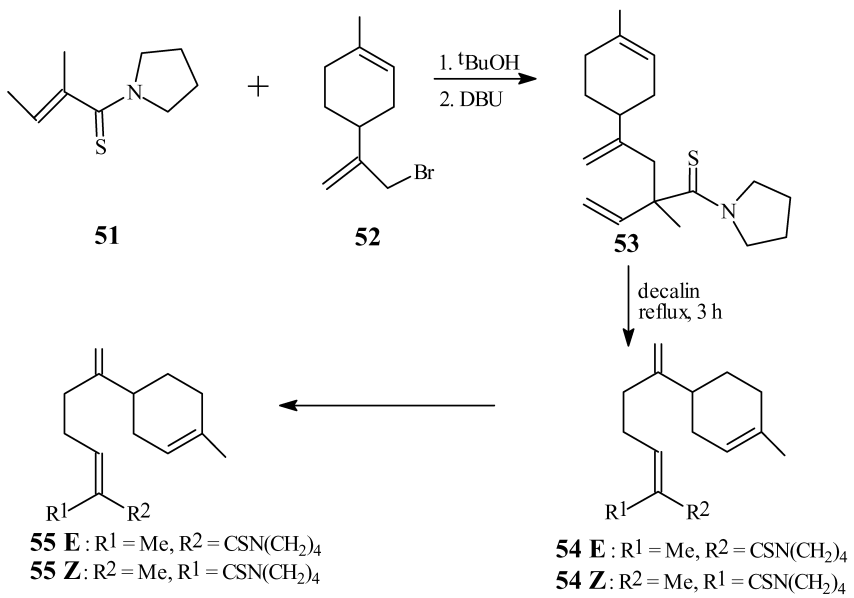
The *S*-allyl ketene dithioacetals **25** undergo[33] a TCR at room temperature or in boiling methylcyclohexane (101°C) to afford the α-allylated dithioesters **26** in good yields and up to 95:5 diastereoselectivities (Scheme 13).

The stereoselectivity, was, therefore, shown to be dependent on the steric bulk of R. By the use of differently substituted allylating agents, it was demonstrated that the stereoselectivity was little affected by the introduction of a substituent at C-5 of the pericyclic nucleus.

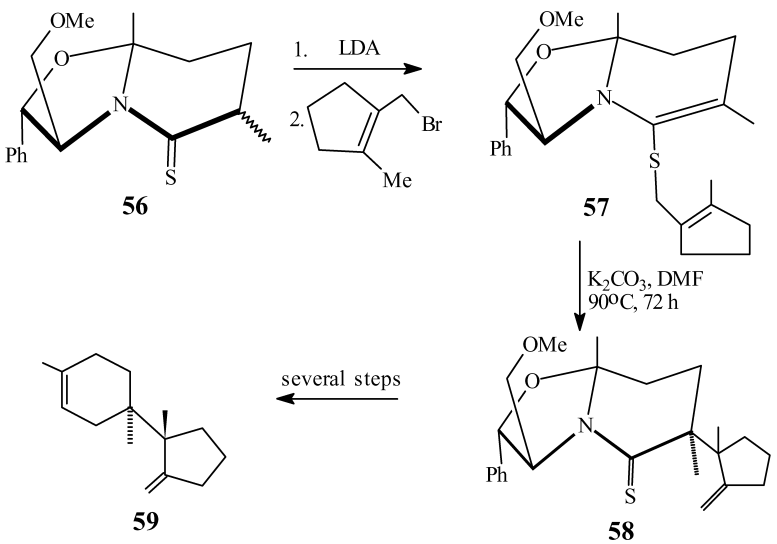
The α-hydroxy *S*-allyl ketene dithioacetals **27** undergo[34] a rapid and highly diastereoselective TCR with preponderant



Scheme 22.



Scheme 23.

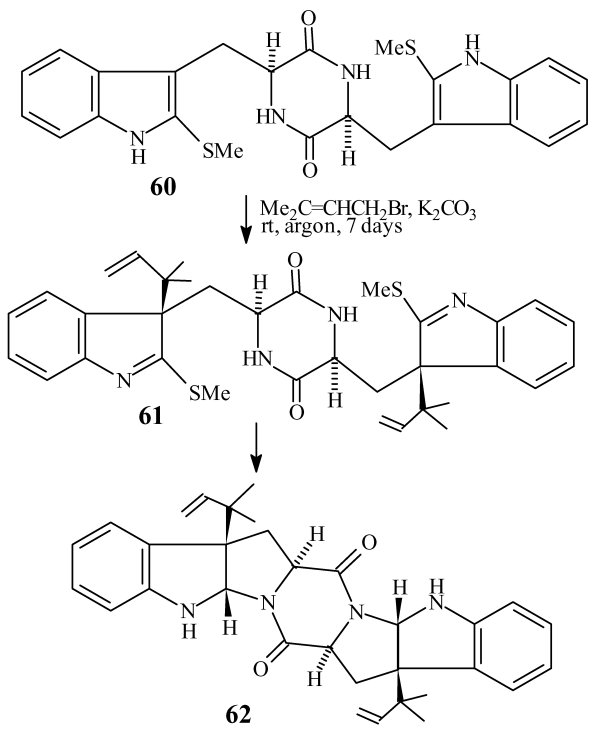


Scheme 24.

formation of the *syn–syn* α-allyl-β-hydroxy-γ-methyl dithioesters **28**. The *anti–syn* isomer **29** was obtained as the minor product (Scheme 14).

The observed diastereoselectivity stems from a stereoelectronic effect conferred by the hydroxyl functionality. The *E*-isomer is found to rearrange more selectively than its *Z*-counterpart. An increase in steric demand of R^1 enhances the *syn*-diastereoselectivity for the *E*-isomer, while, for the *Z*-isomer, it diminishes to a small extent. By this protocol, a carbon framework containing three contiguous stereogenic centres can be built.

The creation of three contiguous stereogenic centres in **31**



Scheme 25.

can also be achieved[35] from the *S*-crotyl-α-hydroxy ketene dithioacetals **30** through a thio-Claisen process (Scheme 15).

Metzner et al.[36] have subjected the *S*-allyl ketene dithioacetals **32** to a TCR at room temperature or at 101°C and have investigated the diastereoselectivity of this sigmatropic process in terms of the two substituents at the stereogenic centre in **33**. They observed a *syn* diastereoselectivity of 75:25 in the product **33** with a methyl and a *t*-butyl group and explained the results by steric factors. With various alkoxy groups, however, a very modest stereoselectivity in favour of the *syn* diastereomer has been achieved (Scheme 16).

The norephedrine-derived bicyclic thiolactam mixture **34** affords[37] the thiolactam **35** through a TCR with crotyl bromide and the ratio of *exo*- and *endo*-isomers of the product **35** is found to be 3:1 (Scheme 17).

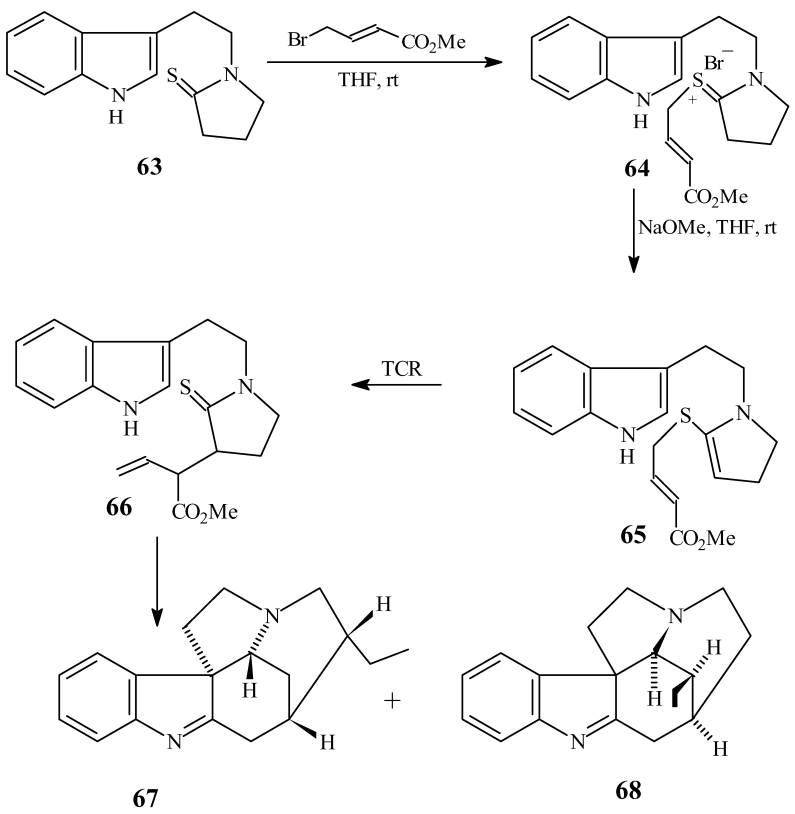
In contrast, the thiolactam **36** undergoes rearrangement with various allylic bromides to give variable diastereoselectivities in the resulting monoallyl derivatives **37** (Scheme 18).

The substitution pattern on the oxazolidine ring of the bicyclic thiolactams is thought to be responsible for the *exo–endo* diastereoselectivity encountered in the above sigmatropic rearrangement, in spite of the apparently remote distance between it and the site of rearrangement.

The *S*-allyl ketene thioaminoacetals **38** rearrange[38] to the bicyclic thiolactams **39** with diastereoselectivities ranging from 3:1 to >99:1, depending on the substitution pattern on the allylic segment (Scheme 19).

The wide variations observed with the rearrangement temperature may be attributed to the non-bonded interactions shown in Figure 1.

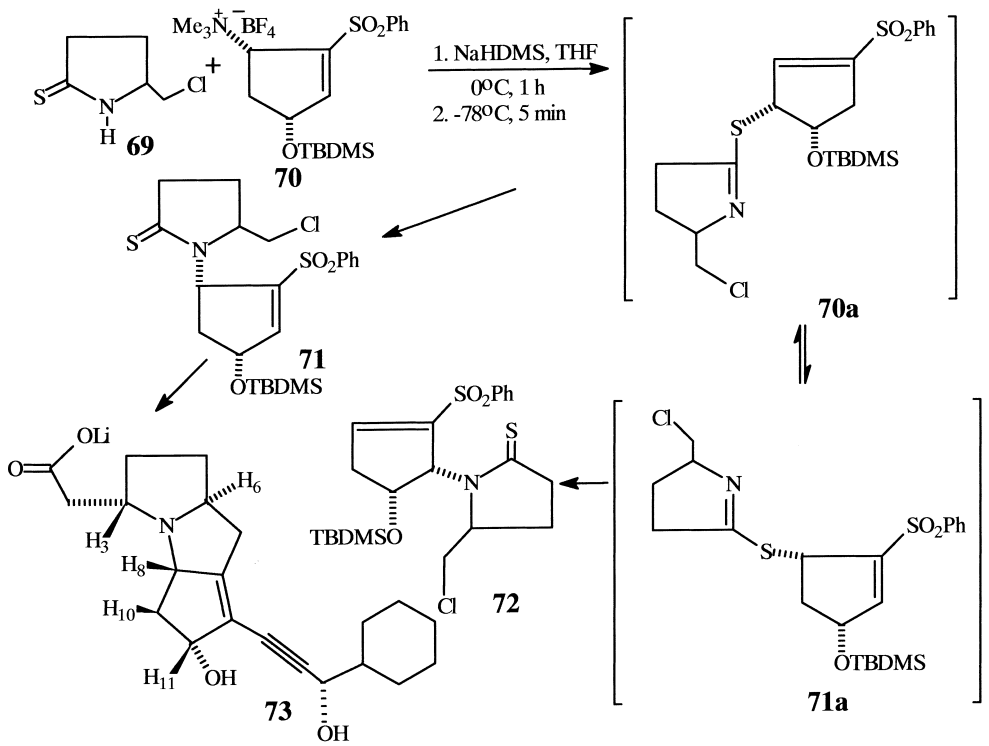
Diastereoselective rearrangement of the zwitterionic species **41** obtained from the reaction between the allyl sulfides **40** and dichloroketene furnishes[39] the thioesters **42**, which are



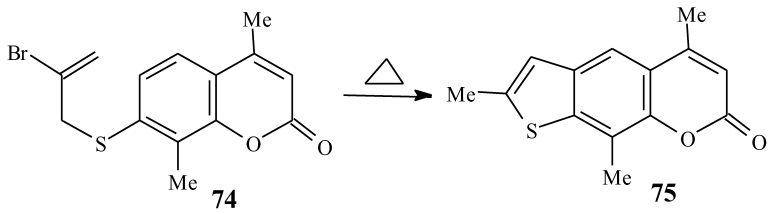
Scheme 26.

obtained in 90–94% diastereomeric excess in favour of the *syn* isomer. The proposed transition state is that with a minimum 1,3-diaxial interaction (Scheme 20).

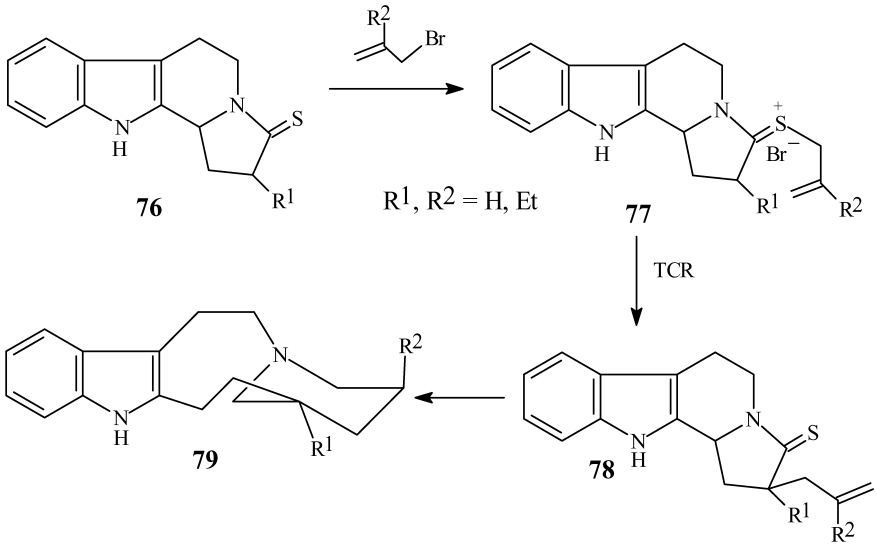
LDA deprotonation of several *N*-arylthioamides containing an axis of chirality along the *N*–C(aryl) bond affords selectively the *Z*-enethiolates, the reaction of which with a variety of allylic halides generates the γ-unsaturated thioamides[40] with excellent diastereoselectivity through a TCR of the incipient *S*-allylketeneaminothioacetals (not



Scheme 27.



Scheme 28.



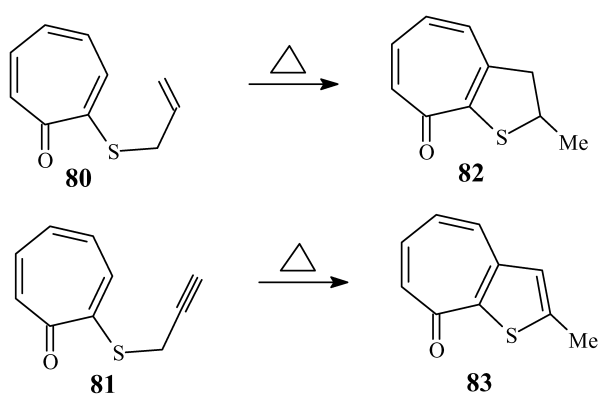
Scheme 29.

isolated). This is the first reported example of an asymmetric Claisen rearrangement involving atropisomeric thioamides.

Methyl-1-benzyl-5-thioxoprolinate **43** gives[41] the corresponding *S*-allyl thioiminium salt (not isolated) on treatment with allyl bromide. Exposure of the crude thioiminium salt to triethylamine in chloroform leads to a facile TCR, with the formation of methyl 4-allyl-1-benzyl-5-thioxoprolinate **44** as a 1.5:1 diastereomeric mixture (4-α **44a**–4-β **44b**). A similar reaction of **43** with propargyl bromide or methallyl chloride affords the corresponding methyl 4-(allenyl/methallyl)-1-benzyl-5-thioxoprolinate (**45a**,**b** and **46a**,**b**) as a diastereomeric mixture (Scheme 21).

Compound **43**, however, fails to react with cyclohexenyl bromide, even in the presence of strong bases like DIPEA or DBU to produce *trans*-4-cyclohexenylproline, a key intermediate in the synthesis of fosenopril, an A C E inhibitor.

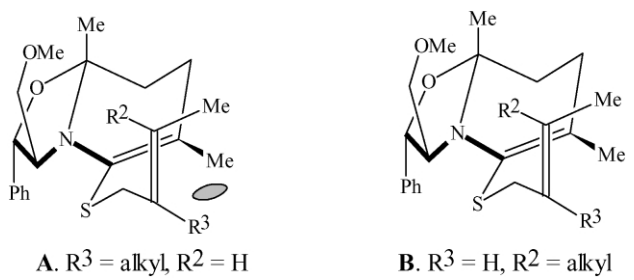
The S-allylated nitrothioacetamides **47** undergo[42] a facile TCR at 45°C in benzene to form the α-allylated thioacetamides **48**. The *N*-nitrothioacetyl derivative of ethyl L-prolinate **49** gives, on allylation, the α-allylthioacetamides **50** as a diastereomeric mixture in which each diastereomer has *cis*/*trans* rotamers. The push–pull system present in structure **47** may be responsible for the facile [3,3] sigmatropic process (Scheme 22).



Scheme 30.

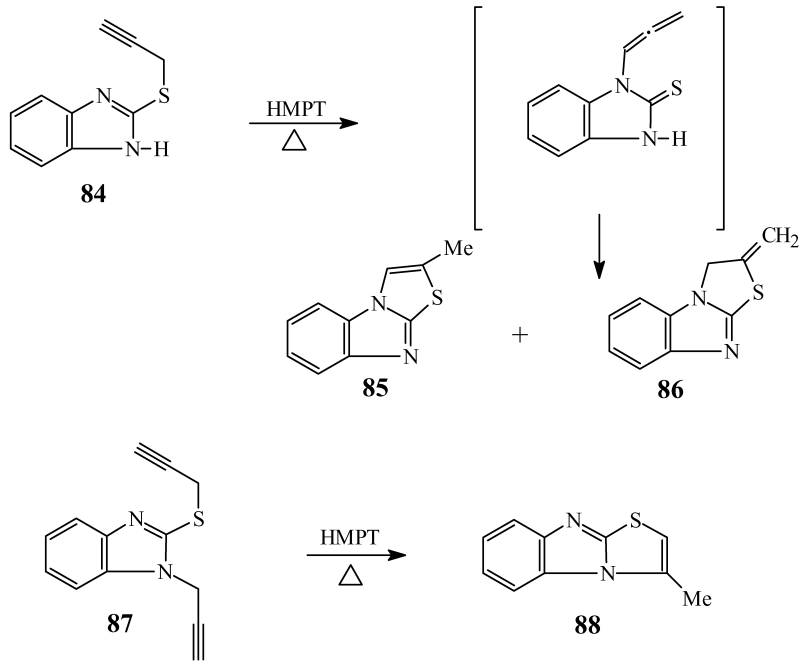
4. Synthesis of natural products

A number of naturally occurring compounds use the TCR in their synthesis. 3-Butenoylthiopyrrolidine **51** reacts[43] with

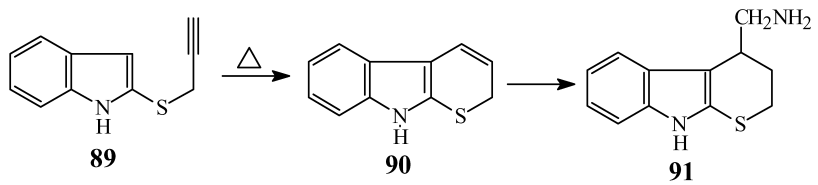


A. R^3 = alkyl, R^2 = H **B**. R^3 = H, R^2 = alkyl

Figure 1.



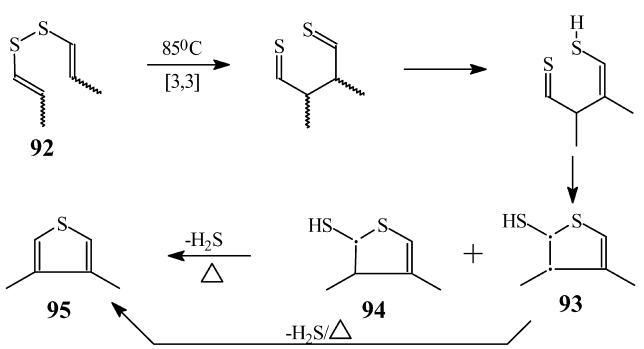
Scheme 31.



Scheme 32.

9-bromolimonene **52** in *t*-butanol in the presence of DBU to furnish the thioamide **53** through a thio-Claisen process. The occurrence of a Cope rearrangement in **53** leads to a diastereomeric mixture of lanceoyl thiopyrrolidine **54** which is finally converted into an (*E*/*Z*) mixture of ethyl lanceolate **55** (Scheme 23).

Trichodiene **59**, a sesquiterpene isolated from the fermentation broth of the mycl elium of *Trichothecium roseum* has been synthesised[44] from the bicyclic thiolactam **58**, which, in turn, is prepared by the TCR of the ketene aminothioacetal **57**. Compound **57** is obtained by the LDA-induced allylation of the thiolactam **56** (Scheme 24).



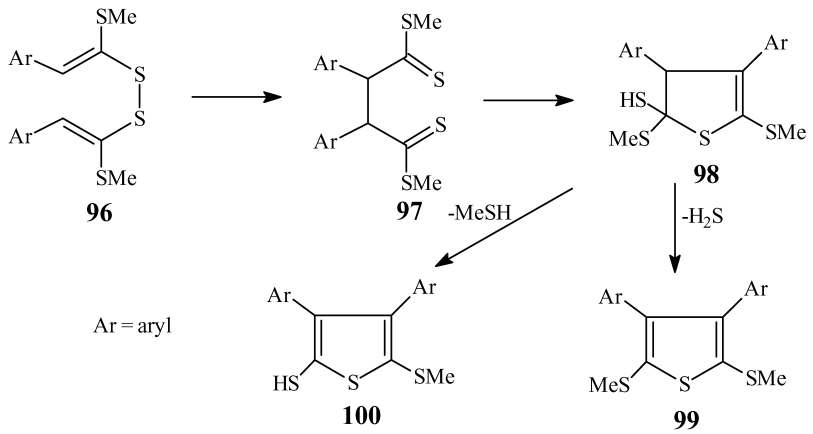
Scheme 33.

(3*S*,6*S*)-3,6-Bis[(2-methylthio-3-indolyl)methyl]-2,5-piperazinedione **60** reacts with prenyl bromide to form the corresponding sulfonium salt (not isolated) which undergoes a TCR to afford the compound **61**. The latter compound is converted[45] into amauromine **62** via reductive desulfurisation with $TiCl_4$–$LiAlH_4$ (1:2) (Scheme 25).

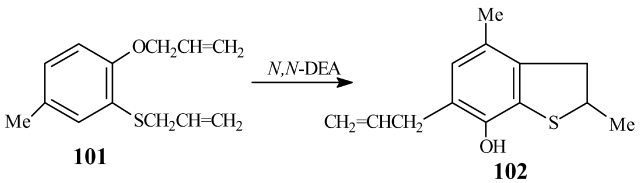
The sulfonium bromide **64**, obtained by the reaction of **63** with methyl γ-bromocrotonate, furnishes **66** through a TCR of **65** in the presence of NaOMe. Compound **66** can be elaborated[46] to tubifoline **67**, a strychnos alkaloid and tubotaiwaine **68**, an aspidospermatidine alkaloid (Scheme 26).

Treatment[47] of 5-chloromethyl-2-thioxopyrrolidone **69** with the ammonium salt **70** gives an isomeric mixture of **71** and **72** through a TCR of the incipient thioimidates **70a** and **71a**, respectively. Exposure of **70** to the neutral thiolactam in CH_2Cl_2, however, exclusively affords the bicyclic thiolactam **71**. This synthetic transformation is used as an integral step in the synthesis of the symchiral-1-azatricyclo [6.3.0.0]undeca-5-enyl prostaglandin I_2 analogue **73** (Scheme 27).

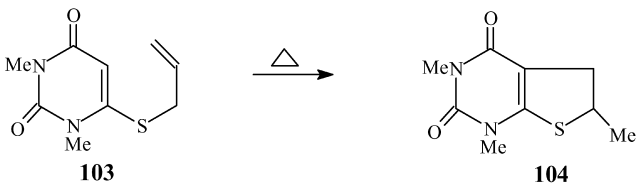
The synthesis[48] of 4,7,9-trimethyl-2*H*-thieno[3,2-*g*]-1-benzopyran-2-one **75**, a psoralen isostere, has been achieved



Scheme 34.



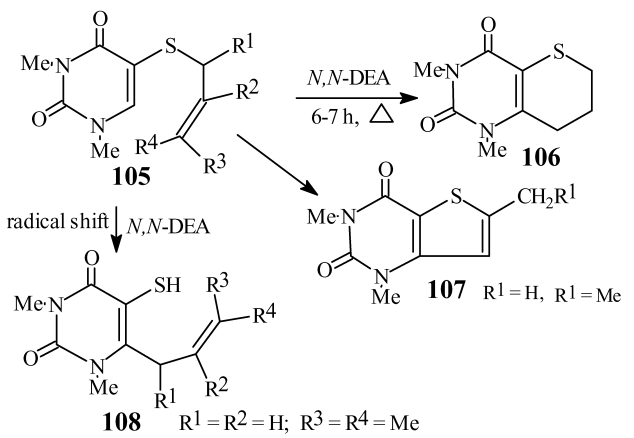
Scheme 35.



Scheme 36.

through a TCR from 7-[(2-bromoallyl)thio]-4,8-dimethyl coumarin **74** (Scheme 28).

The nine-membered indole alkaloids **79** are synthesised[49] using a TCR as one of the necessary steps. Allylation of the tetracyclic thiolactam **76** with allyl bromides generates the sulfonium salts **77**. Treatment of **77** with KOBu^t affords **78** as a mixture of isomers through a thio-Claisen process and **78** is finally converted into **79** (Scheme 29).



Scheme 37.

5. Synthesis of sulfur heterocycles

The TCR provides a very efficient synthetic route to a number of sulfur heterocycles (for a preliminary review, see Ref. 50). 2-(Allylthio)tropone **80** and 2-(propargylthio)tropone **81** give[51] the 2,3-dihydro-(8*H*)-cyclohepta[*b*]thiophene-8-one **82** and (8*H*)-cyclohepta[*b*]thiophene-8-one **83**, respectively. The corresponding γ-substituted allyl derivatives give poor results when subjected to rearrangement, e.g. 2-(prenylthio)-tropone affords isoprene through elimination (Scheme 30).

Balasubramanian et al.[52,53] have subjected 2-propargylthio-benzimidazole **84** to a TCR in hexamethylene phosphorous tribromide (HMPT) to obtain 2-methylthiazolo[2,3-*b*]-benzimidazole **85**, along with the exocyclic benzimidazole derivative **86**. They also obtained 3-methylthiazolo[2,3-*b*]benzimidazole **88** through a depropargylative cyclisation of *N*-propargyl-2-(propargylthio)benzimidazole **87** (Scheme 31).

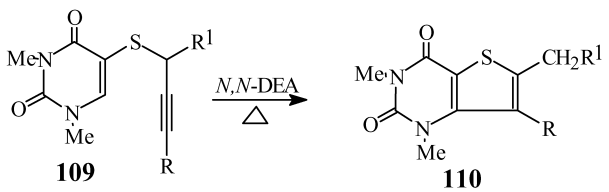
The TCR of indol-2-yl propargyl sulfide **89** furnishes[54] the thiopyrano[2,3-*b*]indole **90**, which is elaborated to 4-aminomethyltetrahydrothiopyran[2,3-*b*]indole **91**, a fused tryptamine analogue (Scheme 32).

The onion oil component, bis(1-propenyl)disulfide **92** affords[55] *cis*- and *trans*-2-mercapto-3,4-dimethyl-2,3-dihydrothiophene **93** and **94**, which can undergo elimination of H_2S on further heating to give 3,4-dimethylthiophene **95** (Scheme 33).

Heating of the disulfides **96** in toluene generates[56] the thiophenes **99** and **100** through the intermediacy of a bisdithioester **97**. Ring closure in **97** leads to the dihydrothiophenes **98**, which may undergo elimination of H_2S or MeSH to furnish the final compounds (Scheme 34).

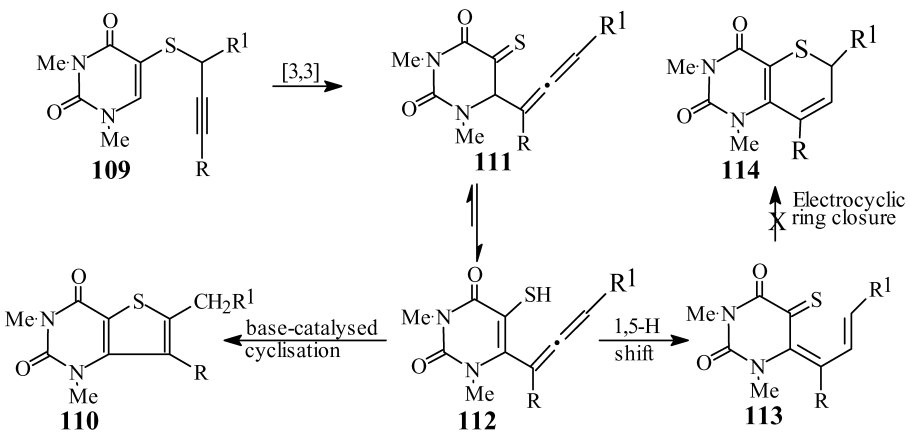
Heating of 1-allyloxy-2-allylthio-4-methylbenzene **101** in *N*,*N*-diethylaniline at 125°C gives[57] 2,4-dimethyl-6-allyl-7-hydroxy-2,3-dihydrobenzothiophene **102**. It is interesting to note that, in this case, both the oxy- and TCRs have occurred simultaneously (Scheme 35).

Thieno[2,3-*d*]pyrimidines such as **104** are synthesised[58] by the TCR of the 6-allylthiouracil derivative **103** (Scheme 36).



R	R^1	R	R^1
H	H	4-$ClC_6H_4CH_2O$	H
H	Me	$C_6H_5CH_2O$	H
CH_2OH	H	4-$OMeC_6H_4CH_2O$	H
CH_2Cl	H	2-$MeC_6H_4CH_2O$	H
2-$ClC_6H_4CH_2O$	H	4-$MeC_6H_4CH_2O$	H

Scheme 38.



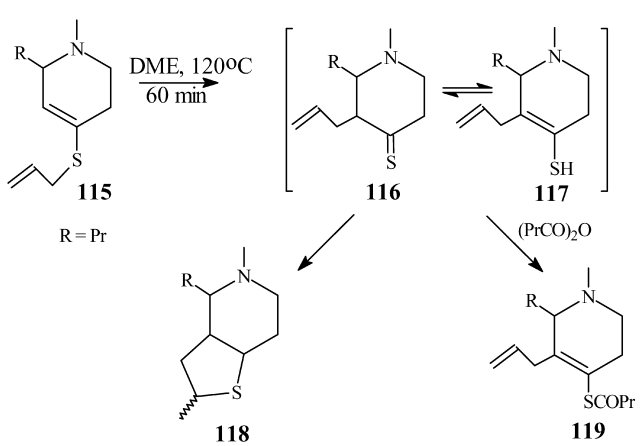
Scheme 39.

The corresponding 5-allylthiouracil derivatives **105**, however, display[59] a more complex product distribution on thermal treatment. Here, the [3,3] sigmatropic pathway is found to be accompanied by a 1,3-radical shift. Compounds **106** and **107** are obtained as a result of [3,3] sigmatropic process whereas compounds **108** are achieved through a 1,3-radical shift (Scheme 37).

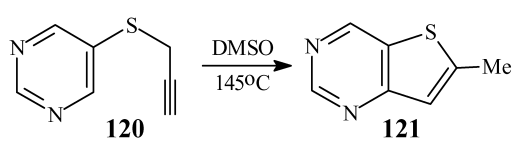
Majumdar et al. have reported[60] the formation of 1,3,6-trialkylthieno[3,2-*d*]pyrimidine-2,4-diones **110** via the thermal sigmatropic rearrangement of the 1,3-dimethyl-5-(prop-2-ynyl)thiouracil derivatives **109** (Scheme 38).

The formation of **110** from **109** can be explained in terms of a [3,3] sigmatropic rearrangement at the vinyl propargyl segment of **109**, leading to the allenyl intermediate **111** which may undergo enolisation to form the enethiol **112**. The base-induced cyclisation of **112** may finally give **110**. Interestingly, the thieno[3,2-*d*]pyrimidines **110** are obtained exclusively, despite the possibility of formation of the thiopyrano[3,2-*d*]pyrimidines **114** through a 6π electrocyclic ring closure of **113**, obtained by a 1,5-H shift in **112** (Scheme 39).

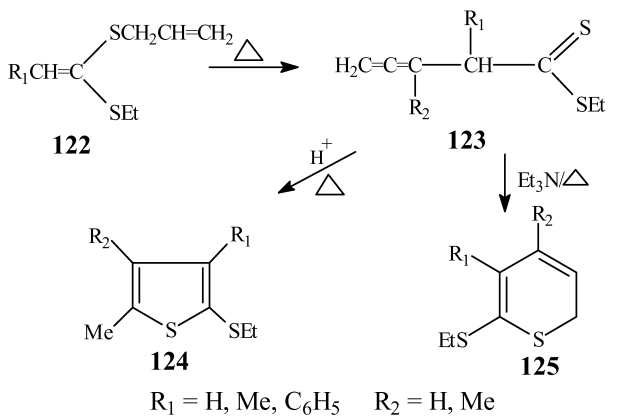
The *S*-allyl sulfide derivative **115**, on heating in dimethoxyethane (DME), affords[61] an epimeric mixture of the thienopiperidine **118** through the enethiol **117**, obtained by tautomerisation of **116**. Evidence for the intermediacy of **117** in this reaction is provided by the formation of the thioester **119** when the reaction is conducted in the presence of added propionic anhydride (Scheme 40).



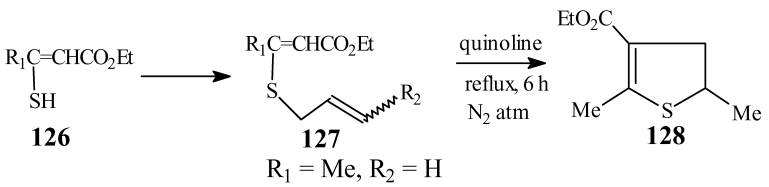
Scheme 40.



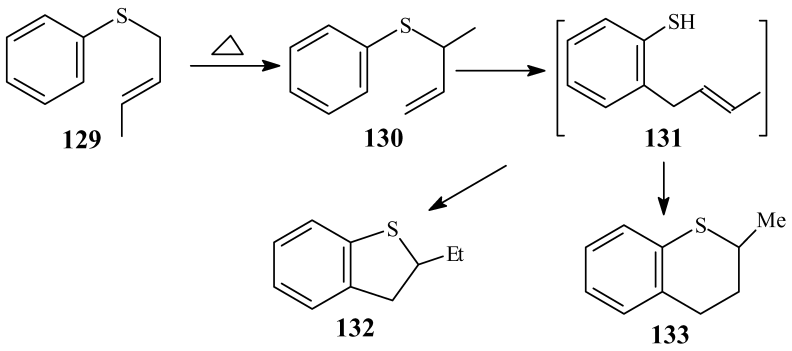
Scheme 41.



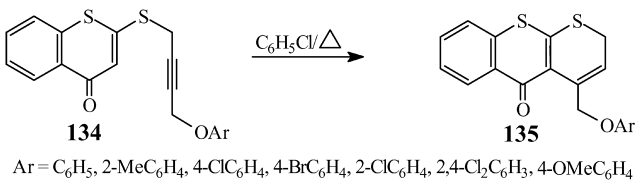
Scheme 42.



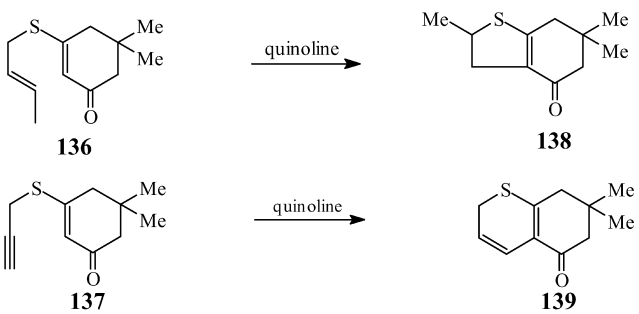
Scheme 43.



Scheme 44.



Scheme 45.



Scheme 46.

The TCR of 5-(2-propenylthio)pyrimidine **120** at 145°C in dimethylsulfoxide (DMSO) gives[62] 6-methylthieno[3,2-*d*]pyrimidine **121** (Scheme 41).

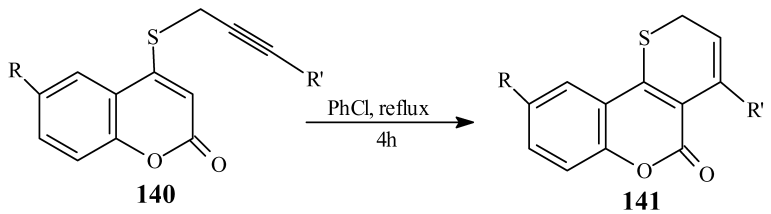
The dithioketeneacetals **122** rearrange on heating under neutral conditions to furnish[7] a mixture of the allenic dithioesters **123**. Some of these compounds undergo cyclisation into the thiophenes **124** and the 2*H*-thiopyrans **125**. Cyclisation of **123** into thiophenes is found to be accelerated by trace amounts of *p*-toluenesulfonic acid, whereas traces of triethylamine strongly favour cyclisation into the 2*H*-thiopyran derivatives (Scheme 42).

Alkylation of the enethiols **126** with allyl bromide or crotyl bromide affords[63] the S-allylated derivatives **127** as a diastereomeric mixture of *E*- and *Z*-forms. The compounds **127** give the dihydrothiophene **128** in refluxing quinoline (Scheme 43).

The TCR of crotyl phenyl sulfide **129** is reported to be preceded by its thioallyl rearrangement to furnish the corresponding 1-methyl isomer **130**. The latter compound undergoes[64] a TCR to 2-crotylthiophenol **131**, which, on cyclisation under the reaction conditions, affords 2-ethyl-2,3-dihydrobenzothiophene **132** and 2-methylthiochroman **133** (Scheme 44).

Majumdar et al. have obtained[65] thiopyrano[2,3-*b*]benzothiopyran-5(2*H*)-one derivatives **135** by a thermal TCR of the sulfides **134** achieved by a phase transfer-catalysed reaction of 4-hydroxydithiocoumarin with 1-aryloxy-4-chlorobut-2-ynes (Scheme 45).

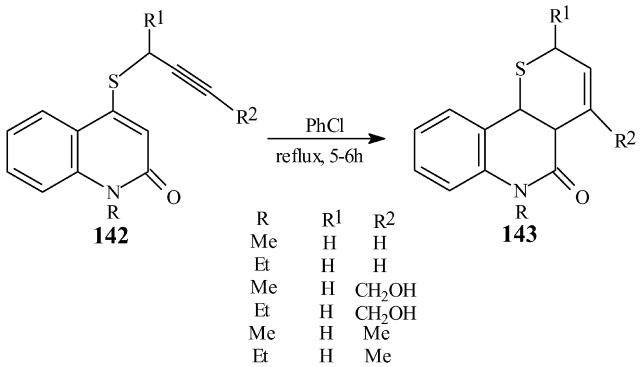
Dimedone-annulated sulfur heterocycles **138** and **139** have been synthesised[66] through a TCR of the dimedone derivatives **136** and **137** respectively (Scheme 46).



140 141

R	R'
H	H
Me	H
H	CH_2Cl
Me	CH_2Cl
H	CH_2OH
H	CH_2OAc

Scheme 47.



142 143

R	R^1	R^2
Me	H	H
Et	H	H
Me	H	CH_2OH
Et	H	CH_2OH
Me	H	Me
Et	H	Me

Scheme 48.

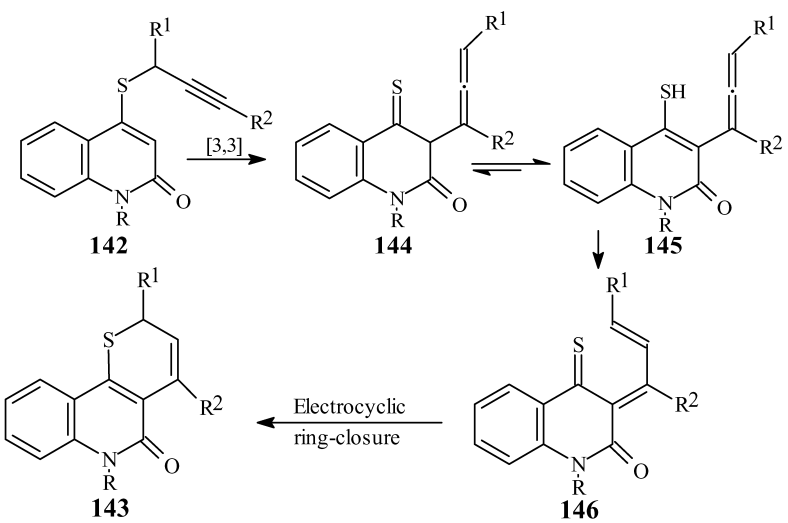
The regioselective synthesis of 2*H*-thiopyrano[3,2-*c*][1]benzopyran-5-ones **141** has been achieved by a TCR of the 4-propargylthio[1]benzopyran-2-ones[67] **140** in refluxing chlorobenzene (Scheme 47).

A number of 1-alkyl-4-prop-2-ynylthioquinolin-2(1*H*)-one derivatives **142** are regioselectively cyclised[68] in refluxing chlorobenzene to the 2*H*-thiopyrano[3,2-*c*]quinolin-5(6*H*)-ones **143** (Scheme 48).

The formation of **143** may be rationalised by an initial [3,3] sigmatropic rearrangement at the vinyl propargyl sulfide unit in **142** to give the allenyl intermediate **144**. Enolisation of **144** may generate the enethiol **145**, which, through a 1,5-H shift followed by electrocyclic ring closure in the resulting **146**, may produce **143** (Scheme 49).

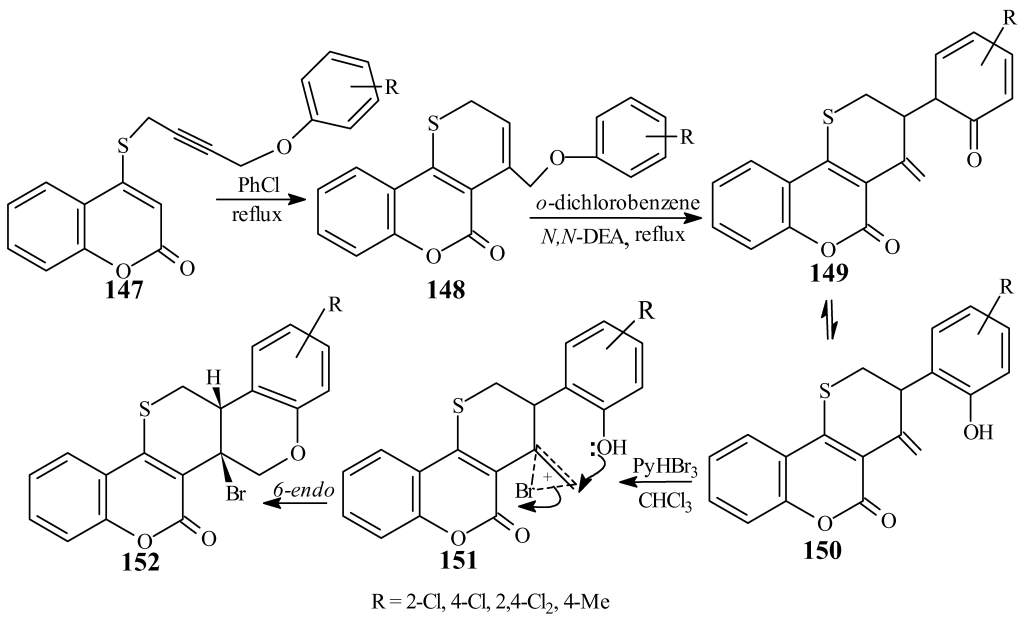
The 4-(4′-aryloxybut-2′-ynylthio)[1]benzopyran−2−ones[69] **147** on refluxing in chlorobenzene afford the 4-aryloxymethylthiopyrano[3,2-*c*][1]benzopyran-5(2*H*)-ones **148** through a TCR. Heating of **148** in *o*-dichlorobenzene in the presence of *N*,*N*-diethylaniline furnishes **150** through aromatisation of **149**. Treatment of the exocyclic derivatives **150** with pyridine hydrotribromide, gives the [6,6]pyranothiopyrans **152** via **151** in almost quantitative yield (Scheme 50).

Thermal rearrangement of the 4-(4′-aryloxybut-2′-ynylthio)-6-methylpyran-2-ones **153** in refluxing chlorobenzene affords the 4-aryloxymethyl-7-methylthiopyrano[3,2-*c*]pyran-5-ones[70] **154**. The compounds **154** are further elaborated to the benzofuro[3,2-*c*]-6a,11a-dihydro-3,11a-dimethylthiopyranopyran-1-ones **155** by a thermal rearrangement in refluxing *o*-dichlorobenzene (Scheme 51).

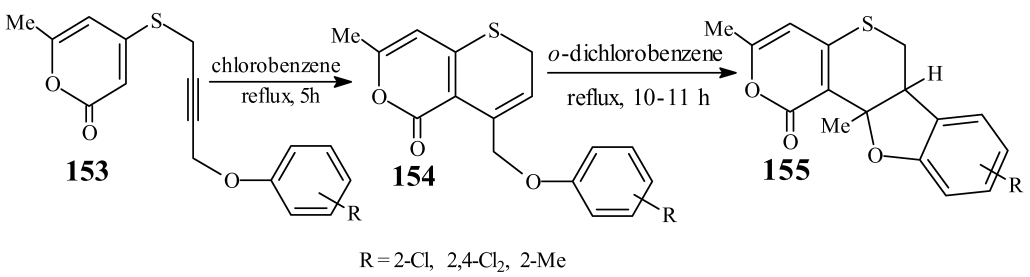


142 144 145 143 146

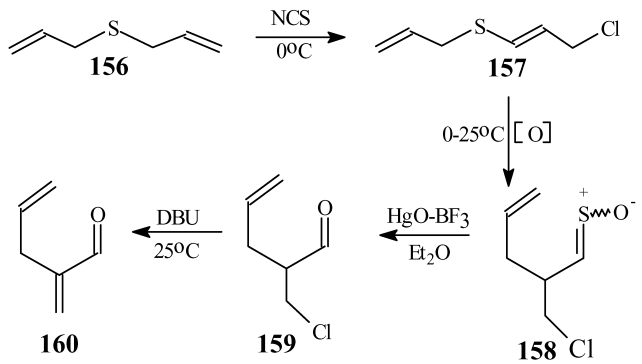
Scheme 49.



Scheme 50.



Scheme 51.

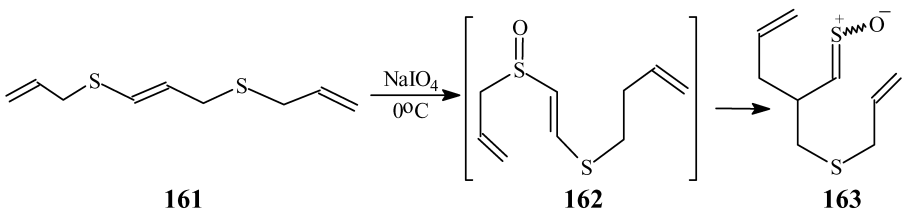


Scheme 52.

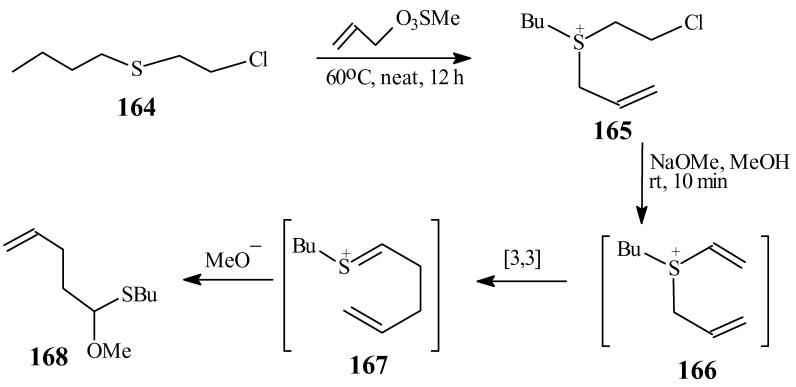
6. Miscellaneous examples

The synthetic utility of the sulfoxide TCR is manifested in the conversion[22] of diallyl sulfide **156** to 2-methylene-5-pentenal **160**. Treatment of **156** with *N*-chlorosuccinimide affords **157**. Oxidation of **157** gives the sulfine **158**. Exposure of **158** to HgO–BF_3 produces **159**, which, on dehydrochlorination, with diazabicycloundecene (DBU) finally gives **160**. The same transformation cannot be achieved from the corresponding sulfide due to the instability of this compound and its rearrangement products under the stringent conditions normally employed for the TCR (Scheme 52).

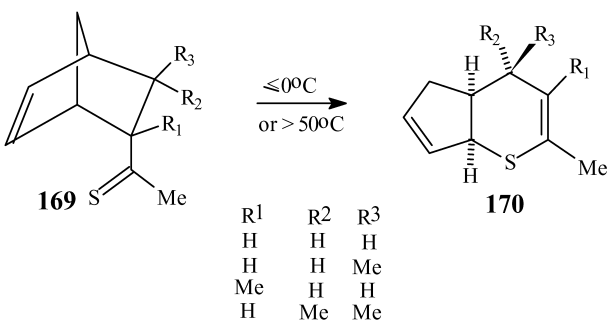
Oxidation of *E*-4,8-dithiaundeca-1,5,10 triene **161** with sodium metaperiodate gives[71] a mixture of *E*-4,8-dithiaundeca-1,6,10-triene-4-oxide **162** and the sulfine **163**,



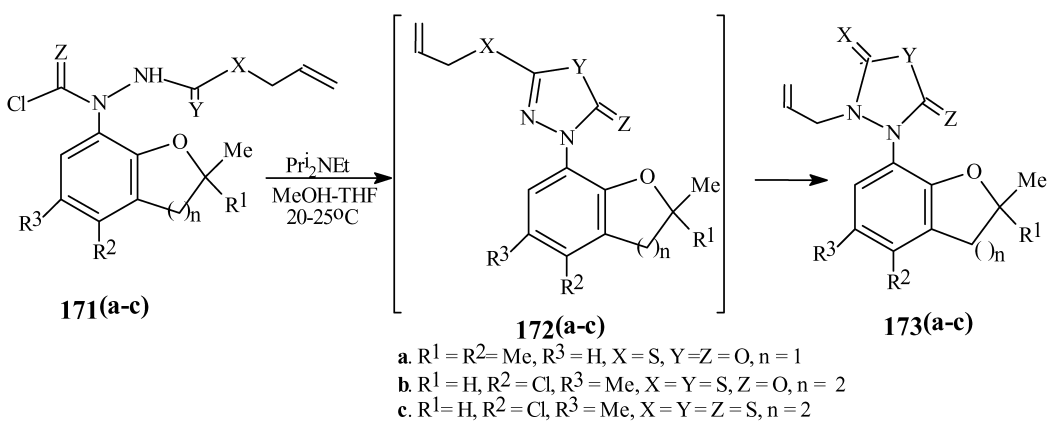
Scheme 53.



Scheme 54.



Scheme 55.

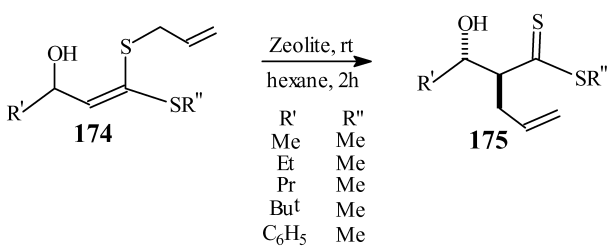


Scheme 56.

presumably via a sulfoxide TCR of **162**. An attempted synthesis of *E*-4,5,9-trithiadodeca-1,7,11-triene-9-oxide, an ajoene isomer, led to a sulfine through a sulfoxide TCR (Scheme 53).

Allylation of the β-chlorosulfide **164** with allyl methanesulfonate affords the β-chlorosulfonium ion **165**. Treatment of **165** with MeONa gives[72] the hemiacetal **168**, presumably via rearrangement of the allyl vinyl sulfonium ion **166**, followed by nucleophilic attack of methoxide on the thionium ion **167** (Scheme 54).

The non-sterically hindered bicyclic thioketones **169** readily undergo a facile retro-thio-Claisen reaction to furnish[73] tetrahydrocyclopenta[*b*]thiopyran **170** stereoselectively. A relief of strain in the bicyclo[2.2.1]heptane may be responsible for the displacement of the equilibrium towards **170**. A highly negative activation entropy compatible with a concerted [3,3] sigmatropic process and a highly ordered tricyclic transition state has been observed (Scheme 55).



Scheme 57.

α,α-Disubstituted thiolactams with various allyl groups are obtained from the reiterative TCR[74] of thiolactams. When the compounds **171a–c** are treated with Hunig's base (Pr^i_2NEt), the compounds **173a–c** are obtained[75] as a result of an extremely facile TCR of **172a–c** (not isolated) (Scheme 56).

Allylic alcohols regioselectively couple[76] with lithium enolates of dithioesters in the presence of 1-chloro-2-methyl-*N*,*N*-tetramethylenepropenylamine under mild conditions to generate the γ,δ-unsaturated dithioesters via a TCR of the incipient *S*-allylic ketenedithioacetals. 3-Allyl-3-cyano-4,7,7-trimethyl-2-thioxo-1,2,3,4,5,6,7,8-octahydroquinolin-5-one is obtained[77] as a thio-Claisen product from 2-allylthio-1,4,5,6,7,8-hexahydroquinoline. Retention of optical activity has been found[78] in the TCR of (−)-*S-trans*-(3-penten-2-yl) 2-thienyl sulfide to the

isomeric (+)-*R*-*trans*-3-(3-penten-2-yl)-2-thiophenethiol. This classifies the reaction as a concerted [3,3]-sigmatropic process. *S*-Allylketenethioaminoacetals obtained from the cyclic *S*-allylmonothiodicarboxamide[79] salts undergo a TCR in the presence of a base to afford the sulfur-to-carbon allylic rearranged products exclusively.

7. Catalysis of the thio-Claisen rearrangement

The catalytic effect on the course of the TCR is much less documented than that of the corresponding oxy- and amino-Claisen rearrangements. Only a few examples are available in the literature. The *S*-allyl-γ-hydroxyketenedithioacetals **174** undergo[80] a facile and diastereoselective TCR into the 2-allyl-3-hydroxydithioesters **175** over different zeolites (Scheme 57).

Zeolites have been found to bring about a remarkable development with respect to the reaction yield and reaction time in comparison to those for the uncatalysed reactions. This zeolite-induced rearrangement gives a preponderance of the *anti* isomer, in contrast to the *syn* isomer obtained predominantly in the uncatalysed reactions. Adsorption of **174** inside the channels of zeolites can occur in such a way that the bulky groups lie away from the catalytic surface. Figure 2 shows the transition state model, the involvement of which may be responsible for the observed diastereoselectivity.

Several palladium and nickel complexes, e.g. $Pd(Ph_3P)_4$, $PdCl_2(MeCN)_2$ and $Ni(COD)_2$, are found[81] to catalyse the TCR of the *S*-allyl-*N*,*S*-keteneacetals **176**. These catalysts hasten the reaction appreciably, but with a sharp decrease in diastereoselectivity (Scheme 58).

The 3-(allylthio)-1,2,4-triazin-5(2*H*)-ones **178** and **180** undergo[82] a TCR to produce **179** and **181**, respectively in the presence of $PdCl_2(PhCN)_2$ under much milder conditions than the uncatalysed reaction (Scheme 59).

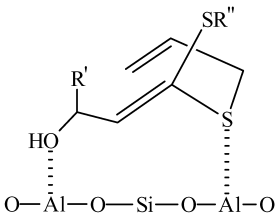
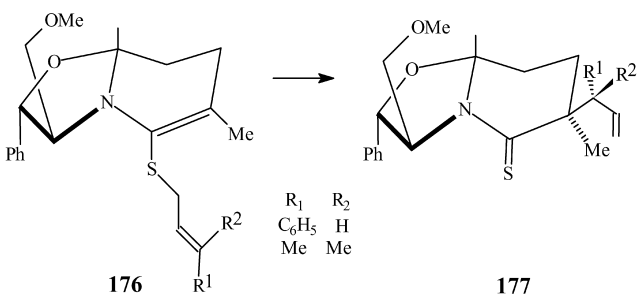
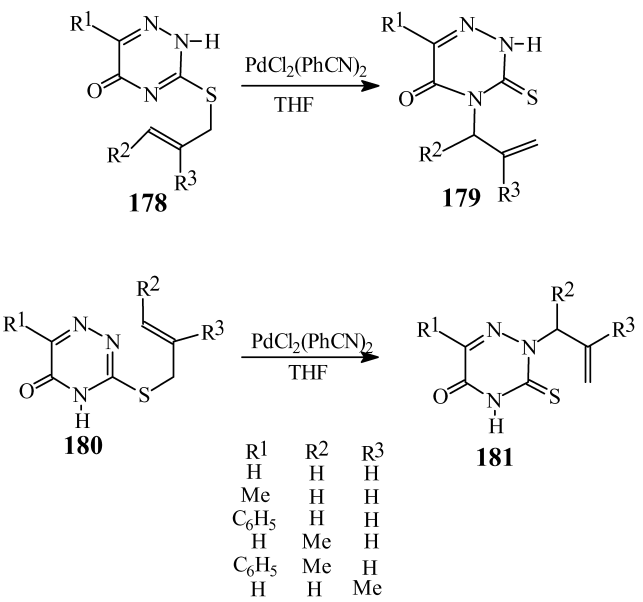


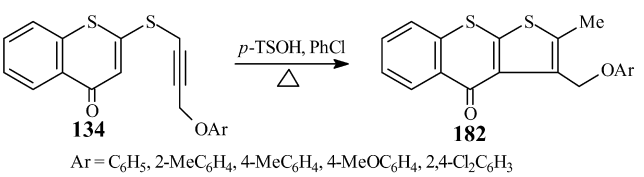
Figure 2.



Scheme 58.



Scheme 59.



Scheme 60.

Catalysis[83] of the TCR of cyclic *S*-allylthioimidates with palladium(II) salts has been investigated.

The acid-induced reaction of (1′,1′-dimethylethyl)thio-1-(*Z*)-alken-3-ols with ethyl orthoacetate occurs via a Claisen rearrangement to furnish the ethyl 3-(1′,1′-dimethylethyl)thio-4(*E*)-alkenoates stereoselectively.[84] The thermal treatment of a number of 2-(4′-aryloxybut-2′-ynylthio)-thiochromen-4-ones **134** in refluxing chlorobenzene in the presence of catalytic amount of 4-toluenesulfonic acid gives the 3-aryloxymethyl-2-methylthieno[2,3-*b*]thiochromen-4-ones[85] **182** (see also Ref. 65). This is an excellent example where acid catalysis has brought about a dramatic alteration in the structural architecture of the product of the TCR (Scheme 60).

8. Conclusions

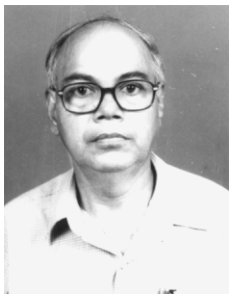
The area of the TCR has not been investigated as thoroughly as those of the corresponding oxy- or amino-Claisen rearrangements. In this review, only recent examples of the utilisation of the TCR in various synthetic strategies has been included. Several stereo-regulated C–C bond formations have involved the use of this reaction. Mechanistic aspects of the rearrangement have been studied in detail. Its synthetic aspects, however, especially the synthesis of sulfur heterocycles and asymmetric induction, still offer enormous challenges to synthetic organic chemists.

References

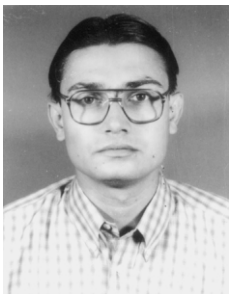
1. Kwart, H.; Hackett, C. M. *J. Am. Chem. Soc.* **1962**, *84*, 1754.
2. Claisen, L. *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 3157.
3. Momose, T.; Yoyooka, N.; Fujii, H.; Yanagino, H. *Heterocycles* **1989**, *29*, 453.
4. Posner, G. H.; Kinter, C. M. *J. Org. Chem.* **1990**, *55*, 3967.
5. Trost, B. M.; Toste, F. D. *J. Am. Chem. Soc.* **1998**, *120*, 815.
6. Ito, H.; Sato, A.; Taguchi, T. *Tetrahedron Lett.* **1997**, *38*, 4815.
7. Schuijl, P. J. W.; Bos, H. J. T.; Brandsma, L. *Rec. Trav. Chim. Pays-Bas* **1969**, *88*, 597.
8. Kwart, H.; Cohen, M. H. *J. Org. Chem.* **1967**, *32*, 3135.
9. Kwart, H.; Evans, E. R. *J. Org. Chem.* **1966**, *31*, 413.
10. Kwart, H.; Cohen, M. H. *J. Chem. Soc. D* **1968**, *319*, 1296.
11. Kwart, H.; George, T. J. *J. Chem. Soc. D* **1970**, 413.
12. Kwart, H.; Schwartz, J. L. *J. Org. Chem.* **1974**, *39*, 1575.
13. Overman, L. E.; Campbell, C. B.; Knoll, F. M. *J. Am. Chem. Soc.* **1978**, *100*, 4822.
14. Kwart, H.; Miles, W. H.; Horgan, A. G.; Kwart, L. D. *J. Am. Chem. Soc.* **1981**, *103*, 1757.
15. Metzner, P.; Pham, T. N.; Vialle, J. *J. Chem. Res. (S)* **1978**, 478.
16. (a) Wehrli, R.; Schmid, H.; Bellus, D.; Hansen, H.-J. *Helv. Chim. Acta* **1977**, *60*, 1325. (b) Wehrli, R.; Bellus, D.; Hansen, H.-J.; Schmid, H. *Chimia (Switz)* **1976**, *30*, 416.
17. Ohno, A.; Ohnishi, Y.; Kito, N. *Int. J. Sulfur. Chem. A* **1971**, *1*, 151.
18. (a) Dewar, M. J. S.; Wade, L. E. *J. Am. Chem. Soc.* **1973**, *95*, 290. (b) Dewar, M. J. S.; Wade, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 4417. (c) Dewar, M. J. S.; Ford, G. P.; Mckee, M. L.; Rzepa, H. S.; Wade, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 5069. (d) Marvell, E. N.; Li, T. H.-C. *J. Am. Chem. Soc.* **1978**, *100*, 883.
19. Anisimov, A. V.; Panov, S. M.; Viktorova, E. A. *Chem. Heterocycl. Compd. (Engl. Transl.)* **1982**, *18*, 912.
20. Anisimov, A. V.; Babaitsev, V. S.; Kolosova, T. A.; Viktorova, E. A. *Chem. Heterocycl. Compd. (Engl. Transl.)* **1982**, *18*, 1032.
21. Anisimov, A. V.; Panov, S. M.; Sizoi, V. F.; Nepogod'ev, S. A.; Viktorova, E. A. *Chem. Heterocycl. Compd. (Engl. Transl.)* **1983**, *19*, 1072.
22. Block, E.; Ahmad, S. *J. Am. Chem. Soc.* **1985**, *107*, 6731.
23. Burrows, C. J.; Carpenter, B. K. *J. Am. Chem. Soc.* **1981**, *103*, 6983.
24. Metzner, P.; Pham, T. N.; Vialle, J. *Nouv. J. Chem.* **1978**, *2*, 179.
25. Metzner, P.; Pham, T. N.; Vialle, J. *Tetrahedron* **1986**, *42*, 2025.
26. Bartlet, P. A. *Tetrahedron* **1980**, *36*, 2.
27. Bennett, G. B. *Synthesis* **1977**, 589.
28. Ziegler, F. E. *Acc. Chem. Res.* **1977**, *10*, 227.
29. Beslin, P.; Lelong, B. *Tetrahedron* **1997**, *53*, 17253.
30. Tamaru, Y.; Mizutani, M.; Furukawa, M.; Kitao, O.; Yoshida, Z. *Tetrahedron Lett.* **1982**, *23*, 5319.
31. Beslin, P.; Perrio, S. *J. Chem. Soc., Chem. Commun.* **1989**, *7*, 414.
32. Tamaru, Y.; Furukawa, Y.; Mizutani, M.; Kitao, O.; Yoshida, Z. *J. Org. Chem.* **1983**, *48*, 3631.
33. Desert, S.; Metzner, P.; Mohamed, R. *Tetrahedron* **1992**, *48*, 10315.
34. Beslin, P.; Perrio, S. *Tetrahedron* **1992**, *48*, 4135.
35. Beslin, P.; Perrio, S. *Tetrahedron* **1993**, *49*, 3131.
36. Desert, S.; Metzner, P. *Tetrahedron* **1992**, *48*, 10327.
37. Watson, D. J.; Lawrence, C. M.; Meyers, A. I. *Tetrahedron Lett.* **2000**, *41*, 815.
38. Devine, P. N.; Meyers, A. I. *J. Am. Chem. Soc.* **1994**, *116*, 2633.
39. Nubbemeyer, U.; Ohrlein, R.; Gonda, J.; Ernst, B.; Bellus, D. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1465.
40. Dantale, S.; Reboul, V.; Metzner, P.; Philouze, C. *Chem. Eur. J.* **2002**, *8*, 632.
41. Jain, S.; Sinha, N.; Dikshit, D. K.; Anand, N. *Tetrahedron Lett.* **1995**, *36*, 8467.
42. Reddy, K. V.; Rajappa, S. *Tetrahedron Lett.* **1992**, *33*, 7957.
43. Tamaru, Y.; Harada, T.; Toshiro, Y.; Yoshida, Z. *J. Am. Chem. Soc.* **1980**, *102*, 2392.
44. Lemieux, R. M.; Meyers, A. I. *J. Am. Chem. Soc.* **1998**, *120*, 5453.
45. Takase, S.; Uchida, I.; Tanaka, H.; Aoki, H.; Itoh, Y. *Tetrahedron* **1986**, *42*, 5887.
46. Takano, S.; Hirama, M.; Ogasawara, K. *Tetrahedron Lett.* **1982**, *23*, 881.
47. Smith, D. C.; Fuchs, P. L. *J. Org. Chem.* **1995**, *60*, 2692.
48. Wellman, G. R. *J. Heterocycl. Chem.* **1980**, *17*, 911.
49. Takano, S.; Hirama, M.; Araki, T.; Ogasawara, K. *J. Am. Chem. Soc.* **1976**, *98*, 7084.
50. Anisimov, A. V.; Viktorova, E. A. *Chem. Heterocycl. Compd. (Engl. Transl.)* **1980**, *16*, 321.
51. Takeshita, H.; Uchida, K.; Mametsuka, H. *Heterocycles* **1983**, *20*, 1709.
52. Balasubramanian, K. K.; Venugopalan, B. *Tetrahedron Lett.* **1974**, 2643.
53. Balasubramanian, K. K.; Venugopalan, B. *Tetrahedron Lett.* **1974**, 2645.
54. Takada, S.; Makisumi, Y. *Chem. Pharm. Bull.* **1984**, *32*, 872.
55. Block, E.; Haizhao, S. *Tetrahedron Lett.* **1990**, *31*, 4999.
56. Larsson, F. C. V.; Brandsma, L.; Lawesson, S. O. *Rec. Trav. Chim. Pays-Bas* **1974**, *93*, 258.
57. Anisimov, A. V.; Girshkyan, A. A.; Gaisina, K. A.; Viktorova, E. A. *Khim. Geterotsikl Soedin* **1994**, *4*, 480.
58. Inoue, H.; Takada, M.; Takashasi, M.; Ueda, T. *Heterocycles* **1977**, *8*, 427.
59. Majumdar, K. C.; Jana, N. K.; Bandyopadhyay, A.; Ghosh, S. K. *Synth. Commun.* **2001**, *31*, 93.
60. Majumdar, K. C.; Jana, N. K. *Synth. Commun.* **2000**, *30*, 4183.
61. Tubery, F.; Grierson, D. S.; Husson, H. P. *Tetrahedron Lett.* **1987**, *28*, 6461.
62. Spada, M.; Klein, R. S.; Otter, B. A. *J. Heterocycl. Chem.* **1989**, *26*, 1851.
63. Dalgaard, L.; Lawesson, S. O. *Tetrahedron* **1972**, *28*, 2051.
64. Danilova, T. A.; Aukharieva, R. G.; Petrov, S. N.; Viktorova, S. Ya.; Grobovenko, E. A. *Chem. Heterocycl. Compd. (Engl. Transl.)* **1981**, *17*, 883.
65. Majumdar, K. C.; Khan, A. T.; Saha, S. *Synth. Commun.* **1992**, *22*, 901.
66. Dalgaard, L.; Lawesson, S. O. *Acta Chem. Scand. B* **1974**, *28*, 1077.
67. Majumdar, K. C.; Ghosh, S. K. *Tetrahedron Lett.* **2002**, *43*, 2115.
68. Majumdar, K. C.; Ghosh, M.; Jana, M.; Saha, D. *Tetrahedron Lett.* **2002**, *43*, 2111.
69. Majumdar, K. C.; Kundu, U. K.; Ghosh, S. K. *Org. Lett.* **2002**, *4*, 2629.
70. Majumdar, K. C.; Kundu, U. K.; Ghosh, S. *J. Chem. Soc., Perkin Trans. 1* **2002**, 2139.

71. Block, E.; Ahmad, S.; Catalfamo, J. L.; Jain, M. K.; Castro, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 7045.
72. Harvey, J. N.; Viehe, H. G. *J. Chem. Soc., Chem. Commun.* **1995**, *22*, 2345.
73. Beslin, P.; Lagain, D.; Vialle, J. *J. Org. Chem.* **1980**, *45*, 2517.
74. Takano, S.; Hirama, M.; Ogasawara, K. *Chem. Lett.* **1982**, 529.
75. Pilgram, K. H.; Skiles, R. D.; Kleier, D. A. *J. Org. Chem.* **1988**, *53*, 38.
76. Fujisawa, T.; Umezu, K.; Sato, T. *Chem. Lett.* **1985**, 1453.
77. Dyachenko, V. D.; Krivokolysko, S. G.; Litvinov, V. P.; Russ, *J. Org. Chem.* **1998**, *34*, 707.
78. Anisimov, A. V.; Panov, S. M.; Egorov, A. M.; Viktorova, E. A. *J. Org. Chem. USSR (Engl. Transl.)* **1984**, *20*, 367.
79. Takahata, H.; Banba, Y.; Mozumi, M.; Yamazaki, T. *Heterocycles* **1986**, *24*, 3347.
80. Sreekumar, R.; Padmakumar, R. *Tetrahedron Lett.* **1997**, *38*, 2413.
81. Watson, D. J.; Devine, P. N.; Meyers, A. I. *Tetrahedron Lett.* **2000**, *41*, 1363.
82. Mizutani, M.; Sanemitsu, Y.; Tamaru, Y.; Yoshida, Z. *J. Org. Chem.* **1983**, *48*, 4585.
83. Takahata, H.; Banba, Y.; Mozumi, M.; Yamazaki, T. *Heterocycles* **1986**, *24*, 947.
84. Lorne, R.; Julia, S. A. *Bull. Soc. Chim. Fr.* **1986**, *2*, 317.
85. Majumdar, K. C.; Ghosh, S. K. *Synth. Commun.* **2002**, *32*, 1271.

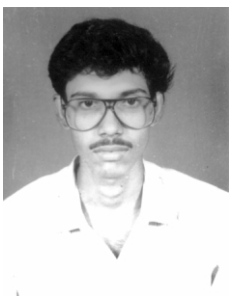
Biographical sketch



Krishna C. Majumdar received his B.Sc. and M.Sc. degrees from the University of Calcutta and the PhD from the University of Idaho, completing his doctoral thesis in 1972 as a teaching fellowship holder under the direction of Professor B. S. Thyagarajan. He was then awarded a research associateship with Professor Thyagarajan at the same University and in 1974 he moved to the University of Alberta as a postdoctoral fellow with Professor R. K. Brown. The following year he joined the group of Professor J. Willian Lown at the same University to study the mode of action of cancer antibiotics. After returning to India (1977) he was with the Birla Institute of Technology and Science as reader for a brief stint. He then moved to the University of Kalyani first as Lecturer (1977) and then as Reader (1984), Professor (1995) and Professor and Head (2003). He also served the Indian Institute of Technology (Kharagpur) for a short period as an associate Professor (1990–1991) and also North Eastern Hill University as a visiting Professor (1996). His research interests centred around synthetic organic chemistry with more than 150 publications mainly based on [1,3], [1,5], [2,3], [3,3] and [3,4]-sigmatropic rearrangements of which Claisen rearrangement is specially notable. Under his guidance, 24 students already received their PhD degrees. He is associated with the discovery of sulfoxide and amine oxide rearrangements for the synthesis of fused thiophenes and pyrroles. His research interests also include radical reactions, design and synthesis of liquid crystals.



Subhojit Ghosh received his B.Sc. and M.Sc. degrees from the University of Kalyani. He obtained the PhD degree in 2002 from the University of Kalyani under the guidance of Professor Krishna C. Majumdar. Presently, he is working as a lecturer in Chemistry in Acharya Prafulla Chandra College. His research interests mainly embrace the synthesis of heterocyclic compounds through oxy-, aza- and thio-Claisen rearrangements and the utilisation of various reagents in the cyclisation of *o*-allyl and *o*-cyclohexenyl phenolic and enolic moieties leading to heterocyclics.



Manish Ghosh obtained his B.Sc. and M.Sc. degrees from the University of Calcutta. He has done his PhD thesis work under the guidance of Professor Krishna C. Majumdar at the Department of Chemistry, University of Kalyani. Presently he is working as a research scientist in Chembiotech Research International. His research interests mainly include synthesis of heterocycles through oxy- and thio-Claisen rearrangements and sulfoxide rearrangement.