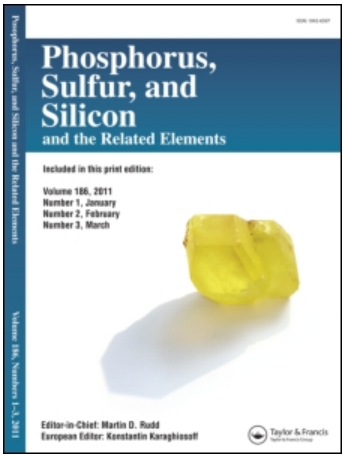


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# THE THIO-CLAISEN REARRANGEMENT

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# THE THIO-CLAISEN REARRANGEMENT

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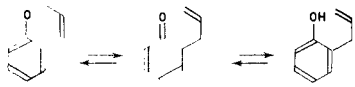
(*Received July 5, 1978*)



## 1 INTRODUCTION

The Claisen rearrangement is an important synthetic method for the preparation of carbonyl compound:[1–4]

and a well known example is the transformation of an *o*-allylation product to *o*-allyl phenol:[5]



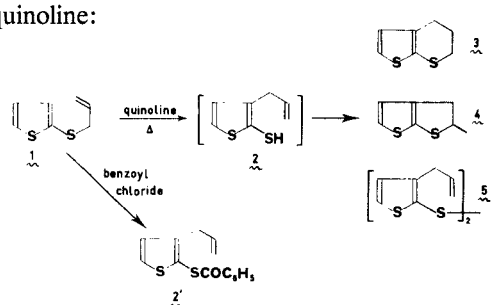
In the sulfur series, this sigmatropic rearrangement[6] has been named Thio-Claisen Rearrangement by Kwart [abbreviation: TCR in this paper].

This review is limited to a number of sulfides and does not include works on ylids.

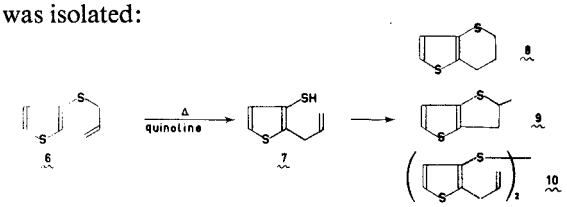
## 2 THIOPHENE DERIVATIVES

### 2.1 *Allyl Sulfides*

It has been shown by Lawesson *et al.*[7] that three main products (**3**), (**4**) and (**5**) were isolated from rearranged 2-allylthio thiophene (**1**). In this procedure, quinoline was heated to 170–180°C and then allyl thienyl sulfide was added. The intermediate (**2**) was not isolated in the course of this reaction. In order to trap this intermediate, the reaction was carried out in benzoyl chloride instead of quinoline:




The products (**8**), (**9**) and (**10**) were isolated from rearranged 3-allylthio thiophene (**6**) and in this case, the intermediate 2-allyl-3-mercaptothiophene (**7**) was isolated:



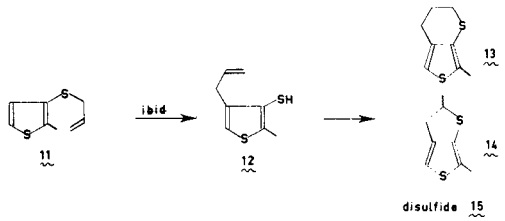

This ring-closure reaction is characteristic of the TCR with thiophenic compounds (see also next section). Thus the TCR often gives two cyclic products: one with a five-membered ring, a second with a six-membered ring. The product distributions of the rearrangement of (**1**) and (**6**) are reported[7] in Table I.

TABLE I

Product distribution of the rearrangement of (**1**) and (**6**)

| | | Conditions | | | |
|---|---|---|---|---|---|
| | | 170°C | 140°C + peroxide | 170°C + peroxide | 190°C + quinone |
| (**1**) → % | (**3**) | 17 | 5 | | 22 |
| | (**4**) | 50 | 17 | | 22 |
| | (**5**) | 33 | 78 | | 56 |
| (**6**) → % | (**7**) | 43 | 62 | 48 | 73 |
| | (**8**) | 38 | 5 | 28 | 16 |
| | (**9**) | 19 | 33 | 24 | 11 |

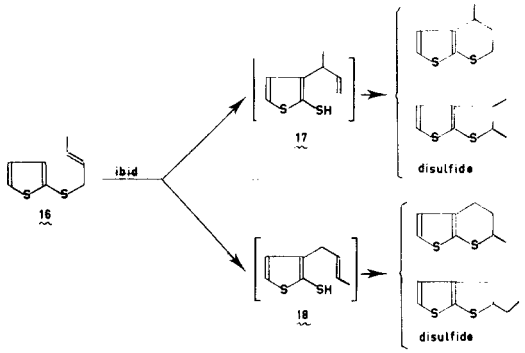
In the same way the rearrangement of 3-allylthio-2-methyl thiophene (**11**) (in which the 2-position is blocked by a methyl group) also undergoes a sigmatropic rearrangement when heated in quinoline and the three products (**13**), (**14**) and (**15**) are isolated:[7]



### 2.2 *Crotyl Sulfides*[7]

With crotyl sulfides, Lawesson *et al.* obtained six products. In this case two intermediates (**17**) and (**18**) are involved and two competitive rearrangements take place: the Claisen sigmatropic shift, and another a radical shift of the crotyl group.

The intermediates (**17**) and (**18**) are not isolated but can be trapped when the reactions are run in benzoyl chloride.




### 2.3 *Propargyl Sulfides*

By heating 2- and 3-(propargylthio)thiophene (**19**) and (**22**) in various solvents at 150–170°C, Brandsma *et al.*[8,9] obtained two cyclic products (**20**) and (**21**) (or **23** and **24**). The first steps in these conversions are Claisen-like rearrangements leading to the allenic compounds (**25a**) (or **25b**). The subsequent ring closure to the corresponding thiophene or thiopyran then take place in a ratio depending on solvent and structure of the added amine (see Table II).

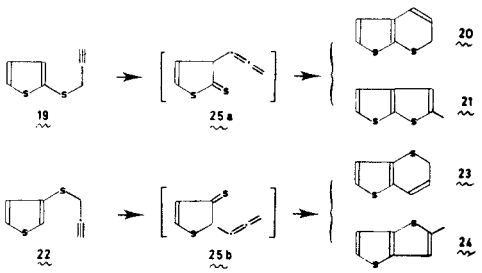



TABLE II

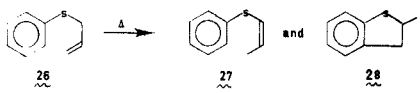
Formation of thienothiophene (**21**) and thienothiopyran (**20**) by heating 2-(propargylthio)-thiophene (**19**) in various solvents in the presence of an amine

| Solvent | Amine | Ratio **21**:**20** |
|---|---|---|
| DMSO, HMPT, DMF quinoline *N*,*N*-diethylaniline | — | 0:100 |
| DMSO | $(n\text{-}C_4H_9)_3N$ | 50:50 |
| HMPT | $(n\text{-}C_4H_9)_3N$ | 5:95 |
| DMSO | Morpholine | 45:55 |
| HMPT | Morpholine | 40:60 |
| DMSO | Piperidine | 75:25 |
| DMSO | $(i\text{-}C_3H_7)_2NH$ | 75:25 |
| HMPT | $(i\text{-}C_3H_7)_2NH$ | 40:60 |
| DMF | $(i\text{-}C_3H_7)_2NH$ | 2:98 |
| Quinoline | $(i\text{-}C_3H_7)_2NH$ | 0:100 |
| DMSO | $(n\ C_3H_7)_2NH$ | 75:25 |

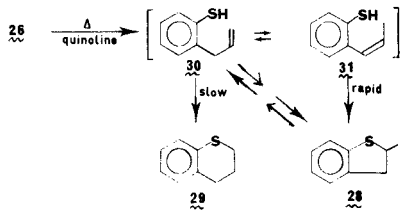
## 3 THIOPHENOL AND THIONAPHTHOLS DERIVATIVES

### 3.1 *Sulfides With One Carbon–Carbon Double Bond*

In 1930 Hurd *et al.*[10] studied the thermal rearrangement of allyl aryl sulfides. However, most of the results obtained in this field have been obtained by Kwart *et al.* In 1962 they published the TCR of sulfide (**26**):[11]




Meyers *et al.*[12] studied the same reaction independently and obtained two cyclic products (**28**) and (**29**). They proposed the following scheme:

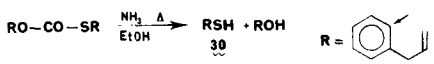



In 1966 Kwart *et al.*[13] showed that in a typical TCR medium, allyl phenyl sulfide (**26**) gave a mixture of

TABLE III

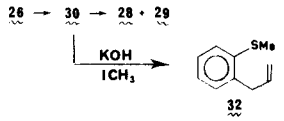
| Identity of fraction isolated | Composition % 6 h 217–241°C in quinoline | 6 h 220°C in 2,6-dimethylaniline |
|---|---|---|
| Allyl phenyl sulfide (**26**) | 0 | 12 |
| 2-Methyl-1-thiacoumaran (**28**) | 40 | 47 |
| 1-Thiachroman (**29**) | 37 | 33 |
| Polymeric material | 19 | 6 |
| Thiophenol | 4 | 4 |

cyclic products consisting of thiachroman (**29**) and thiacoumaran (**28**). The composition of the product mixtures resulting from a rearrangement of (**26**) under some typical reaction conditions is shown in Table III. Besides, in the same publication,[13] Kwart *et al.* prepared *o*-allylthiophenol (**30**) according to the following reactions:

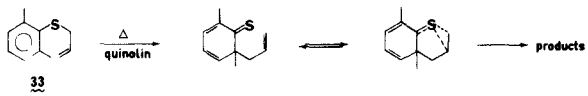


On dissolving such prepared (**30**) in dry quinoline and heating it at 217–241°C for 6 h under nitrogen, they obtain a reaction mixture consisting of nearly four parts of thiachroman (**29**) to one part of thiacoumaran (**28**); under exactly the same reaction conditions, allyl phenyl sulfide (**26**) was converted to a mixture consisting of nearly identical amounts of (**28**) and (**29**) (see Table III).

These results establish that *o*-allyl thiophenol (**30**) was the intermediate of the TCR; moreover this intermediate was trapped in the course of a typical TCR according to the following scheme:[14]



In this field, TCR has also been studied with different solvents and starting materials[15] (Table IV). An interesting example is shown below for the thermal rearrangement of (**33**), in which thiiran formation is postulated.[17]



In 1976 Gopalan *et al.*[18] reported a facile catalysed TCR of α-arylthiomethyl acrylic acids (**34**) when heated with triethylamine in *o*-dichlorobenzene. Thus they prepared the unknown thiochroman-3-carboxylic acids (**35**):

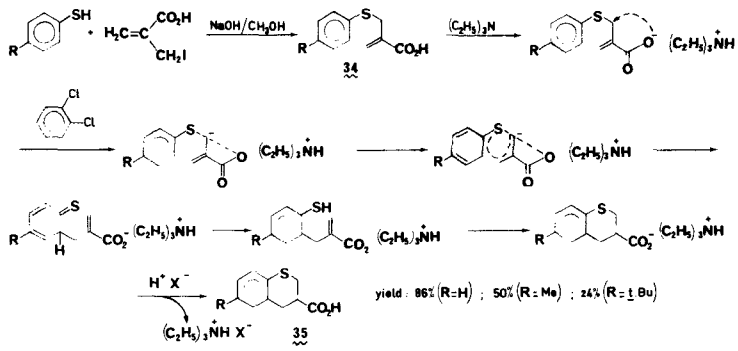
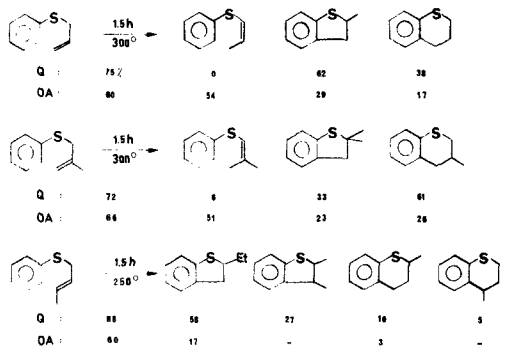
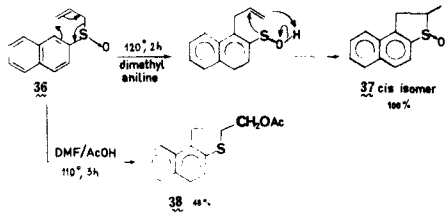


TABLE IV

Results of the thermolysis of different sulfides in quinoline (Q) and octanoic acid (OA)



Finally we would like to mention briefly the communication of Maksumi *et al.*[19] on the TCR of allyl aryl sulfoxides. They invoke a [3,3]sigmatropic rearrangement of the sulfoxide (**36**) and intramolecular *cis* addition of the resulting sulfenic acid by a six-electron electrocyclic process:



### *3.2 Sulfides With One Carbon–Carbon Triple Bond*

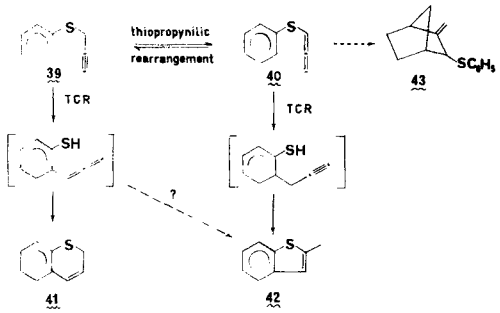
The course of the oxy-Claisen rearrangement of acetylenic ethers has been the subject of several investigations.[4,20,21] The TCR of propynyl phenyl sulfide (**39**) was reported in 1970.[22] The thermolysis of (**39**) in quinoline solution at 200°C yields mainly three rearrangement products (**40**), (**41**) and (**42**)

TABLE V

Product composition (%) in thermolysis of (**39**)

| Products | Reaction conditions | |
|---|---|---|
| | 5 h 200°C | 0.5 h 250°C |
| (**40**) | 24.5 | — |
| (**41**) | — | 39.5 |
| (**42**) | 71 | 47.5 |

[the component (**40**) is essentially trapped by addition of an equivalent of cyclopentadiene to the quinoline solution and isolating the Diels–Alder adduct (**43**)] (Table V):




Also reported was the rearrangement of but-2-ynyl phenyl sulfide (**44**) under the same conditions.[22] This reaction is slower and leads to a more complex product mixture, which is reminiscent of the homologous TCR of crotyl phenyl sulfide[15] (Table VI).

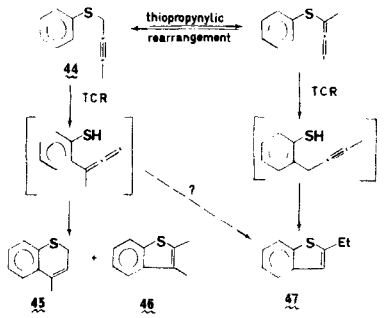


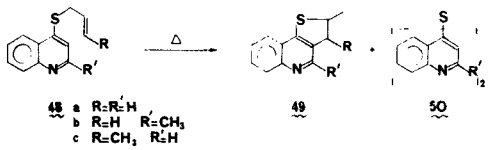

TABLE VI

Product composition (%) in thermolysis of (**44**)

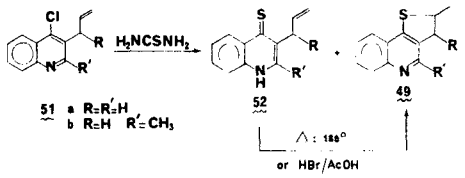
| Products | Reaction conditions | |
|---|---|---|
| | 24 h 200°C | 4 h 270°C |
| (**44**) | 4 | 2 |
| (**45**) | 0.5 | 5 |
| (**46**) | 17.5 | 15 |
| (**47**) | 35 | 46 |

## 4 QUINOLINE DERIVATIVES

Allyl quinolyl sulfides and crotyl quinolyl sulfides were studied in 1966 by Makisumi.[23] Heating (**48**) at 200°C for 1 h without solvent results in the formation of two compounds (**49**) (69–75%) and (**50**) (2–5%).

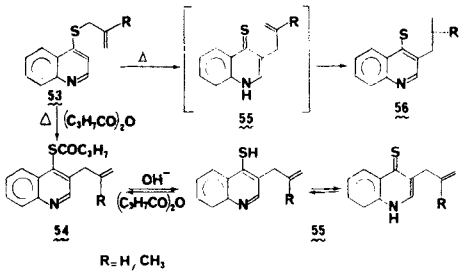



Moreover the reaction of 3-allyl-4-chloroquinoline (**51a**) or 3-allyl-4-chloroquinaldine (**51b**) with thiourea in boiling ethanol for 1 h affords a 60% yield of (**52**) and a 30% yield (**49**). (The structure of the TCR product (**49**) was confirmed by independent synthesis from (**52**), via treatments with HBr–AcOH, or by heating (180°C).) These results suggest that the normal Claisen product (**52**) may be an intermediate in the TCR of (**48**):

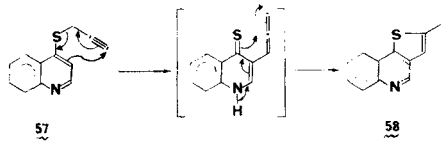



In 1969, Makisumi *et al.*[24] presented a definitive evidence for the intermediacy of (**52**) suggesting that the mechanism involving a thiiran intermediate (proposed by Kwart *et al.*[25]) is erroneous.

To trap an intermediate, 3-allyl-4 (1H)-quinolinethione (**55**) during the rearrangement reaction, Makisumi *et al.*[24] heated at 200°C for 2 h allyl quinolyl sulfide (**53**) in the presence of butyric anhydride and obtained the butyric ester (**54**). The hydrolysis product of (**54**) is identical with authentic (**55**) and the butyric ester obtained by treatment of (**55**) with butyric anhydride is also identical with (**54**). These facts suggested to Makisumi *et al.* that compound (**55**) is the sole intermediate in the TCR of allyl quinolyl sulfides:

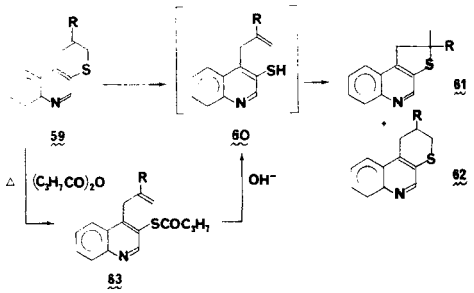


With the propargyl sulfide (**57**) heated at 200°C for 2 h in dimethylaniline, the same authors[24] obtained 2-methyl thieno [3,3-*c*]quinoline (**58**) (yield: 80%):



**57** **58**

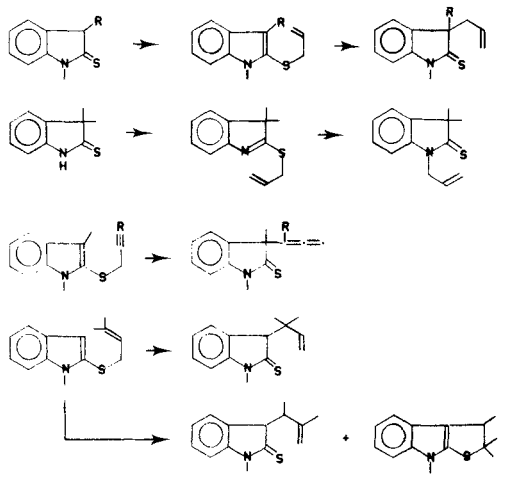
The thermal rearrangement of sulfide (**59**) affords 2,2-dimethyl-1,2-dihydrothieno [2,3-*c*]quinoline (**61**) and 2-methyl-2,3-dihydro-1H-thiopyrano [2,3-*c*]-quinoline (**62**). Makisumi *et al.*[26] believe that these products are formed by the cyclization of the intermediate (**60**) produced from (**59**) by the [3,3]sigmatropic rearrangement of aromatic allyl sulfides:



**59** **60** **61** **62** **63**

## 5 INDOLE DERIVATIVES

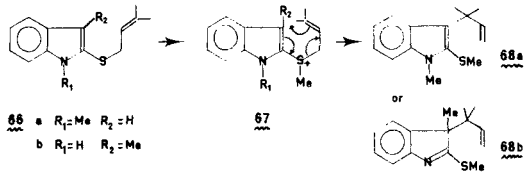
The thermal rearrangement of allyl and prop-2-ynyl-2-indolyl sulfides was studied in 1970.[27] This study is very interesting because Bycroft *et al.* do not generally obtain cyclic products, but thioketones. These results confirm the postulated intermediates in the reaction of Kwart and Makisumi. The following reactions have been studied:



3-(allylthio) indole (**64**) rearranges on heating to yield 2-allyl-3-indolethiol (**65**):[28]

**64** **65**

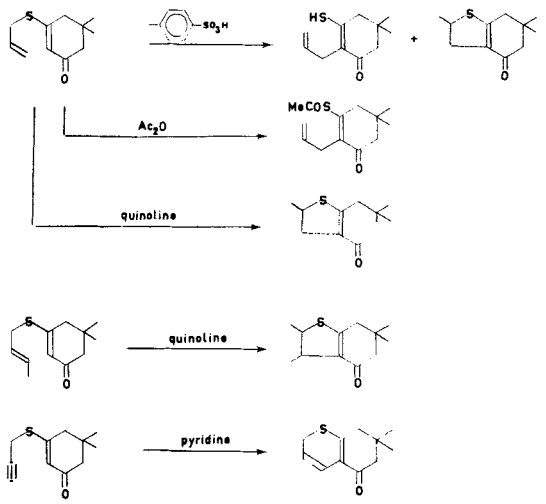
The methyl sulphonium cations (**67a**) and (**67b**) derived from (**66a**) and (**66b**) readily rearrange at room temperature and give the *S*-alkyl derivatives (**68a**) and (**68b**) respectively.[29]



**66** a $R_1$=Me $R_2$=H; b $R_1$=H $R_2$=Me **67** **68a** **68b**

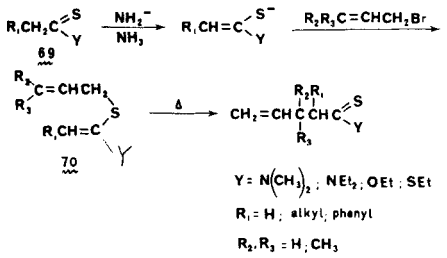
## 6 DIMEDONE DERIVATIVES

In 1974 Lawesson *et al.*[30] investigated the thermal and photochemical rearrangements of dimedone derivatives. They observed a formation of two types of cyclic products: one with a five-membered ring, a second with a six-membered ring:

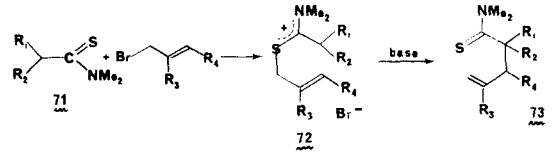


## 7 THIOAMIDE DERIVATIVES

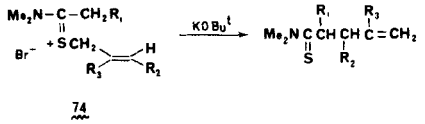
In 1968, Brandsma *et al.*[31] studied the TCR of substituted allyl vinyl sulfides (**70**) obtained by alkylation of thioamides, thionesters or dithioesters (**69**):



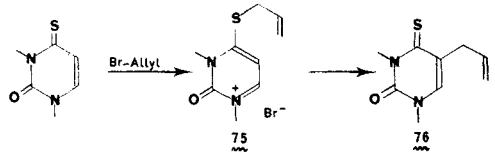
Thus, the thioamides (**71**) and allyl bromides afford the salts (**72**) in excellent yields. Treatment of solutions of (**72**) in acetonitrile with diisopropylethylamine (or HNa in THF) furnishes the new thioamides (**73**) in 60–80% yield.[32]



The same reaction has been described by Takano *et al.*[33] In this case the method involves stirring the sulphonium bases (**74**) with KOBu$^t$ in THF at room temperature (Table VII).



The first example of TCR in pyrimidine chemistry was reported in 1975. Thus the compound (**75**) rearranges readily to yield the corresponding 5-allyl-4-thiouracil isomer (**76**):[34]



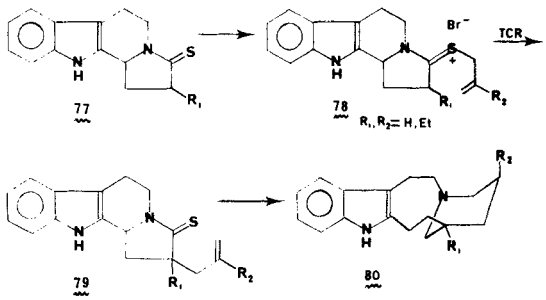
Synthesis of the nine-membered indole alkaloids (**80**) by the TCR has also been studied.[35]

TABLE VII

Reaction of the sulfonium bases (**74**) with KOBu$^t$ in THF at seven temperatures

| $R_1$ | $R_2$ | $R_3$ | % yield |
|---|---|---|---|
| H | H | H | 82.1 |
| H | Me | H | 52.5 |
| H | H | Et | 55.3 |
| $CH_2$=CH–$CH_2$ | H | H | 56.3 |
| $CH_2$=CH–$CH_2$ | Me | H | 32.3 |
| CHMeCH=$CH_2$ | H | H | 58.8 |
| $CH_2C(Et)$=$CH_2$ | H | Et | 40.9 |

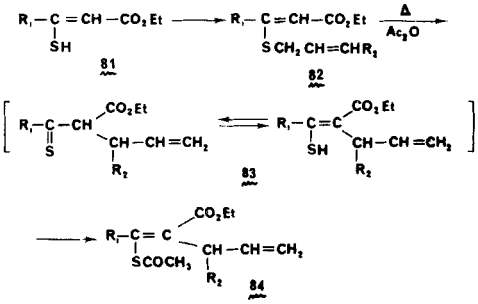
In this procedure the tetracyclic thiolactam (**77**) was treated with 2-bromomethyl-1-ene to give the salt (**78**) which on exposure to KOBu$^t$ underwent the rearrangement to afford (**79**) in 81.8% yield (mixture of isomers).



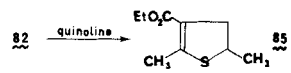
## 8 β-THIONOESTER DERIVATIVES

### 8.1 *Acyclic Compounds*

*Allyl and crotyl sulfides* The TCR of some enethiol derivatives was performed in 1972 by Lawesson *et al.*[36] The alkylation of enethiols (**81**) with allyl or crotyl bromides, gives the *S*-alkylated products (**82**) (a mixture of *E* and *Z* forms). In refluxing, acetic anhydride at 140°C the sulfides (**82**) give the products (**84**) in good yields. The postulated intermediates (**83**) were not isolated in the course of this reaction.



In refluxing quinoline under nitrogen for 6 h, the sulfide (**82**) ($R_1$ = Me, $R_2$ = H) gives the heterocyclic product (**85**) (yield: 29%) as the only isolated product.

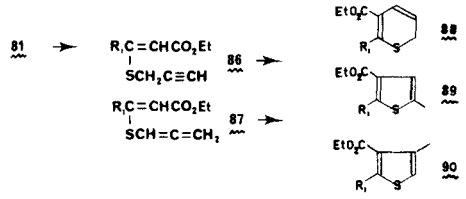


*Propargyl sulfides*[36] The alkylation of (**81**) with propargyl bromide results in a mixture of acetylenic and allenic compounds (**86** and **87**). The TCR of these compounds in various solvents gives one, two,

TABLE VIII

| Starting products | Solvent | T°C | Hours | (88) | (89) | (90) |
|---|---|---|---|---|---|---|
| $R_1$ = Me (86) | Pyridine | 160 | 4 | 92 | 8 | — |
| | $NEt_3$ | 89 | 4.5 | 66.5 | 33.5 | — |
| $R_1$ = $C_6H_5$ (86) | Quinoline | 180 | 1.5 | 64 | 36 | — |
| | $NEt_3$ | 89 | 3.25 | — | 100 | — |
| | $Ac_2O$ | 160 | 3 | — | 100 | — |
| $R_1$ = Me (87) | Quinoline | 180 | 5 | 22 | 53 | 8 |
| | Quinoline | 180 | 1.5 | 34 | 36 | — |
| | $AC_2O$ | 140 | 20 | — | 44 | 56 |
| $R_1$ = $C_6H_5$ (87) | Pyridine | 160 | 0.5 | — | 84 | 15 |

or three heterocyclic derivatives (**88, 89, 90**) (Table VIII).

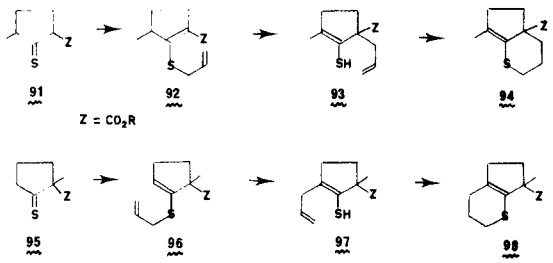


## 8.2 *Alicyclic Compounds*

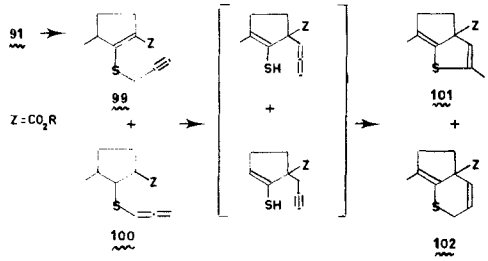
Alicyclic $\beta$-thioxo esters[37] react with alkyl halides to give conjugated *S*-alkylated compounds.[38]

The TCR of these sulfides has been studied with different types of starting compounds.

Thus the alkylation of (**91**) (or **95**) with allyl bromide gives one *S*-alkylated product (**92**) (or **96**). By heating this derivative (distillation or VPC) it is possible to isolate the enethiol (**93**) (or **97**) which cyclizes to product (**94**) (or **98**) slowly at room temperature and quickly at 180°C:[38]

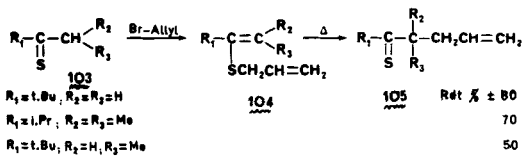


The same reaction can be obtained with crotyl derivatives. However, it was observed that the crotyl sulfides rearrange more slowly than allyl sulfides which is suggestive of a concerted mechanism. Alicyclic $\beta$-thioxo ester (**91**) also reacts with propargyl bromide to give two compounds: an acetylenic derivative (**99**) and an allenic derivative (**100**). These two *S*-alkylated products can be isolated but not separated by VPC. Indeed, by VPC (or distillation) they produce the heterocyclic compounds (**101**) and (**102**). In this last case the postulated enethiolic intermediates are not isolated:[38]

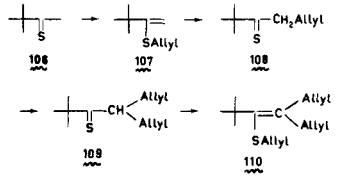


## 9 THIOKETONE DERIVATIVES[39,40]

Aliphatic thioketones (**103**) react with allyl bromide to give allylthio compounds (**104**) in good yields (90%). These sulfides have a strong tendency to undergo TCR and by distillation it is possible to isolate new thioketones (**105**):



These thioketones (**105**) are stable compounds and the corresponding cyclic products are not obtained. The same reaction is observed with thiocamphor as a starting material. In the course of this investigation the behaviour of "rearranged thioketones" (**105**) has been studied. Thus thiopinacoline (**106**) reacts with allyl bromide and the allylthio compound obtained (**107**) produces allylic thioketone (**108**). This last product, by a second TCR gives the new stable thioketone (**109**). Finally (**109**) reacts with allyl bromide and furnishes the sulfide (**110**) which is stable under Claisen rearrangement conditions.

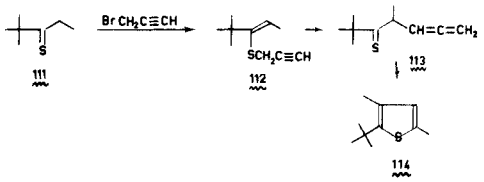


The same behaviour can be observed with crotyl derivatives. However, yields are lower and crotyl sulfides rearrange more slowly than the allyl sulfides.

Aliphatic thioketones (e.g. **111**) react also with propargyl bromide and give propargyl thio compounds (like **112**). This sulfide is very unstable and it rapidly furnishes the new allenic thioketone (**113**). This thioketone is not as stable as the allylic thio-

ketones (**105**); the spectra of this product can, however, be recorded.

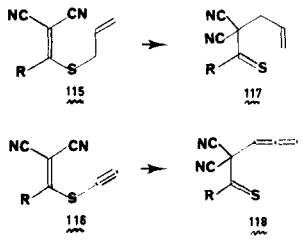
The allenic thioketone gives the heterocyclic compound (**114**) on distillation.



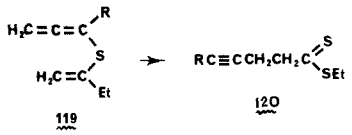
## 10 VARIOUS ACYCLIC SULFIDES

### *10.1 Monosulfides*

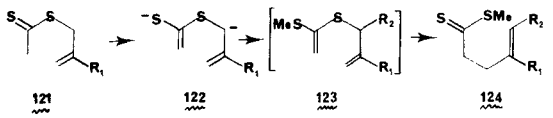
*Preparation of a thiocarbonyl compound* The investigation of the thermal behaviour of the dicyano sulfides (**115**) (or **116**) has been studied by Hartke *et al.*[41] They find that these compounds when heated rearrange into the thiocarbonyl compounds (**117**) (or **118**):



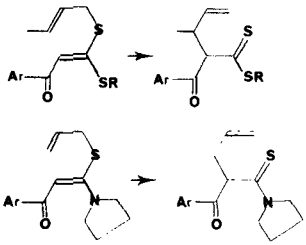
The TCR of the allenic ketene dithioacetals (**119**) produces the acetylenic dithioesters (**120**). These conversions took place at 80–100°C:[42]



Treatment of the dithioester (**121**) with sec-butyllithium gives a dianion (**122**) which by addition of an alkyl halide and methyl iodide followed by TCR affords a new dithioester (**124**) via the ketene thioacetal (**123**):[43]

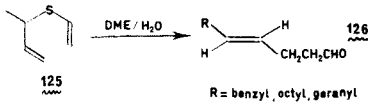


Finally, we can mention the two following conversions:[44,45a]



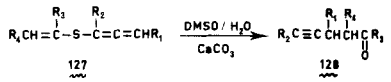
For a study of a TCR in silicon/sulfur series see Ref. 45b.

*Preparation of a carbonyl compound* Oshima *et al.*[46] described in 1973 a general two-step sequence which permits the stereoselective conversion of a dienic compound (**125**) to the *trans*-$\gamma,\delta$-unsaturated aldehyde (**126**). This reaction involves the TCR of the starting materials:

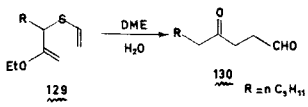


Concerning this latter reaction, Brandsma *et al.*[47] mentioned in 1974, that they were unable to reproduce these results; they obtained only about 25% yield.

In the same publication, Brandsma *et al.*[47] studied the [3,3]sigmatropic rearrangement of sulfides (**127**) at 125–135°C in DMSO and water. This reaction gives aldehydes or ketones (**128**) in moderate yields (Table IX).



Synthesis of 4-oxodecanol (**130**) has also been reported.[48] The TCR is carried out by dissolving (**129**) in DME/Water and heating at reflux for 12 h (66% yield):

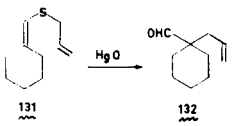


When (**131**) is heated at 190°C for 10 min in the presence of red mercuric oxide 1-allyl-1-cyclo-

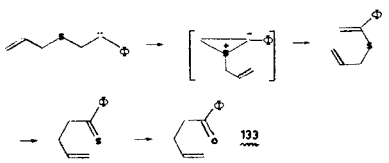
TABLE IX

| $R_1$ | $R_2$ | $R_3$ | $R_4$ | Yield (%) (**128**) |
|---|---|---|---|---|
| H | $C_4H_9$ | H | H | 40 |
| H | $C_4H_9$ | H | Me | 42 |
| Me | $C_4H_9$ | H | H | 40 |
| Me | $C_4H_9$ | Me | H | 54 |

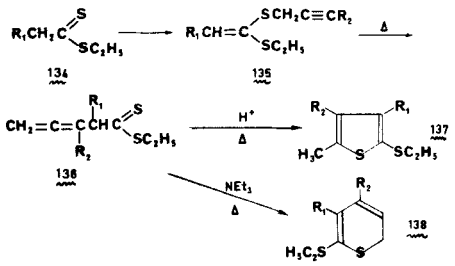
hexanecarboxaldehyde (**132**) can be obtained in 82% yield.[49] We think that this reaction is the first described in this field.



The intramolecular participation of the sulfide linkage in the reactivity of carbene and diazoalkanes has been studied by Ojima *et al.*[50,51] In this study they have obtained the ketone (**133**) and propose the following scheme:



*Preparation of a heterocyclic product* (via a thiocarbonyl compound) The dithioacetals (**135**) can be obtained in a moderate yield by adding dithioesters (**134**) to one equivalent of potassium amide in liquid ammonia and pouring the resulting solution into an excess of the bromoalkyne $R_2$–C≡$CCH_2Br$. On heating in neutral conditions a number of compounds (**135**) rearrange to give allenic dithioesters (**136**). However, some of these compounds are not isolated in a pure state, because they rearrange into thiophenes (**137**) and 2H-thiopyrans (**138**).[52]



Traces of triethylamine strongly accelerate the conversion of (**136**) into derivatives of 2H-thiopyran (**138**) and formation of thiophenes (**137**) is facilitated by trace amounts of *p*-toluenesulfonic acid in the reaction medium.

From 1968 to 1972 Brandsma *et al.*[53–56] studied the thermal rearrangement of acetylenic–ethylenic sulfides. Thus 1-alkynyl-allenyl sulfides (**139**) leads to thioketene (**140**), proposed as an intermediate, which can be trapped by adding a secondary aliphatic amine to the reaction medium. The adduct (**141**) can be isolated in reasonable yields (Table X).

TABLE X

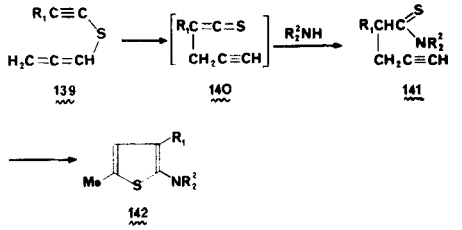
Thermal rearrangement of acetylenic–allenic sulfides (**139**)

| Isolated compounds | $R_1$ | $R_2$ | Yield % |
|---|---|---|---|
| (**141**) | Me | Et | 47 |
| (**141**) | Me | Pr | 53 |
| (**141**) | Et | Pr | 60 |
| (**142**) | Me | Et | 38[a]; 59[b] |
| (**142**) | Et | Et | 66[a]; 58[b] |
| (**142**) | Et | Pr | 72[a]; 62[b] |

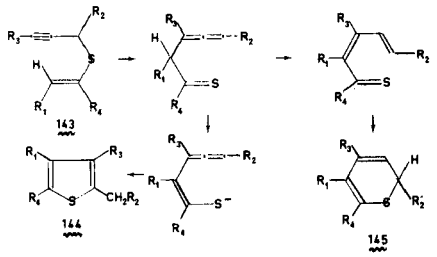
Cyclization of the thioamide (**141**) to trisubstituted thiophenes (**142**) is carried out in two ways:

—with a catalytic amount of $KOBu^t$ (a)

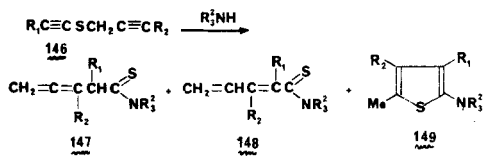
—by heating in HMPT at about 240°C (b).



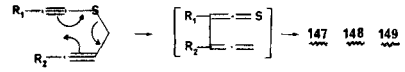
Thiophenes (**144**) and 2H-thiopyran (**145**) can be prepared by thermal rearrangement of propargyl vinyl sulfides (**143**) according to the following scheme:[54,56,57]



Another type of TCR can be observed by thermal rearrangement of 1-alkynyl-2-alkynyl sulfides (**146**) in the presence of dialkylamines or dialkylphosphines:[57,58]



The following mechanism has been suggested:[58]



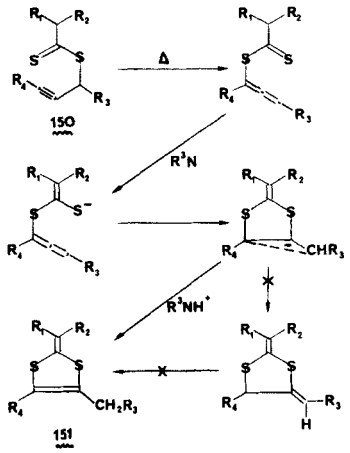
Some of these results appear in Tables XI and XII.

TABLE XI

Rearrangement of EtC≡C–S–$CH_2$–C≡CH in the presence of 200% excess of $Et_2NH$ in various solvents

| Solvent | % (**147**) | % (**148**) | % (**149**) | Total yield |
|---|---|---|---|---|
| $Et_2NH$ | 70 | 24 | 6 | 60 |
| DMSO | 12 | 82 | 6 | 64 |
| $CH_3CN/Et_2O$ | 39 | 56 | 5 | 58 |
| Pentane | 73 | 20 | 7 | 35 |
| EtOH | 22 | 73 | 5 | 49 |
| MeOH | 24 | 76 | 4 | 46 |
| DMSO/MeOH | 18 | 74 | 6 | 45 |
| DMSO/$NH_4Cl$ | 4 | 81 | 5 | 50 |

2-alkynyl alkanedithioates (**150**) rearrange at 130–140°C in the presence of catalytic amount of $EtN(iPr)_2$ to 1,3-dithiole derivatives (**151**). Although the intermediates have not been isolated, Brandsma *et al.*[59] propose the following mode of formation for (**151**) (see also Ref. 60).



Finally, unsaturated sulfonic acid derivatives (**153**) are obtained upon heating allyl vinyl sulfones (**152**)[61] in EtOH/pyridine at 160–170°C.

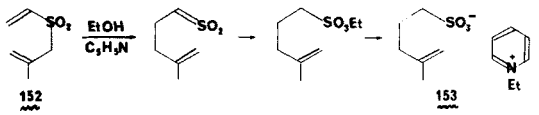


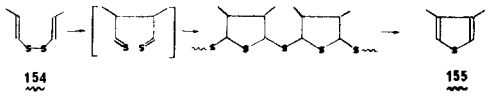
TABLE XII

Rearrangement of (**146**) in $Et_2NH$ at 60°C

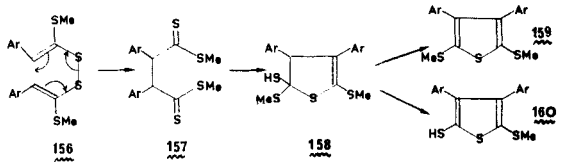
| $R_1$ | $R_2$ | % (**147**) | % (**148**) | % (**149**) | Total yield |
|---|---|---|---|---|---|
| Me | Me | 5 | 90 | 5 | 62 |
| Me | Et | 6 | 89 | 5 | 60 |
| Et | Me | 5 | 91 | 4 | 62 |
| Et | Et | 4 | 92 | 4 | 59 |
| $CH_2$=CMe | Me | 4 | 93 | 7 | 60 |
| Me–C≡C | Me | 4 | 95 | 5 | 51 |

### *10.2 Disulfides*

Disulfides (**154**) upon heating with potassium hydrogen sulfate at 150–200°C undergo a vigorous decomposition with evolution of hydrogen sulfide. So Brandsma *et al.*[62] obtain by distillation 3,4-dialkyl thiophene (**155**) in about 60% yield and they propose the following scheme:



Heating the disulfide (**156**) in toluene to 100°C for 3 h affords the thiophenes (**159**) and (**160**). The authors[63] think that the formation of (**159**) and (**160**) can be accounted for by assuming a [3,3] sigmatropic rearrangement resulting in the bis dithioester (**157**), which undergoes ring closure to a dihydrothiophene (**158**), from which $H_2S$ or MeSH are eliminated to give the final compounds:



## 11 CONCLUSION

### *11.1 General Remarks*

The TCR can be observed in various experimental conditions:

— with or without solvent

— in basic, acid, or neutral medium

— at room temperature or at high temperature

— with or without irradiation.

The TCR can produce either heterocyclic products or new thiocarbonyl compounds and it is a very important synthetic method in organic sulfur chemistry.

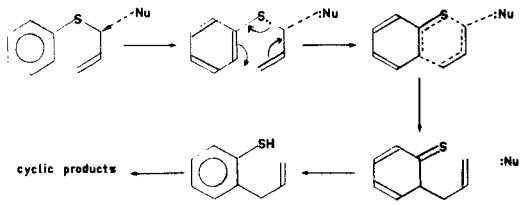
Different compounds in which one possible position is blocked by an alkyl group, also undergo a TCR in another free position (e.g. **11** and **95**).

### *11.2 Mechanism*

The mechanism of the TCR has been studied only in the thiophenol series by Kwart *et al.*[64] These authors present evidence substantiating a thiophenolic intermediate in the TCR of allylic phenyl sulfides and

think that the TCR is susceptible to nucleophilic catalysis.

Mechanism of the TCR: Kwart and Schwartz.[64]




However, in a number of cases, TCR is brought about thermally without solvent or catalyst. These observations of different laboratories are consistent with a concerted mechanism. Recently Vialle *et al.*[65] have demonstrated that the TCR of 3-allylthio-2,4-dimethylpent-2-ene involves a thermal [3,3]sigmatropic process and that the reverse reaction (retro Claisen) proceeds simultaneously and though a pericyclic process is generally assumed for the Claisen rearrangement, these authors do not exclude a biradicaloid transition state (as for the Cope rearrangement[66,67]).

For a discussion on the competitive [3,3]sulfur shifts during the TCR see Ref. 68.



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