THIO-CLAISEN REARRANGEMENT IN THE SYNTHESIS OF SULFUR-CONTAINING HETEROCYCLIC COMPOUNDS (REVIEW)

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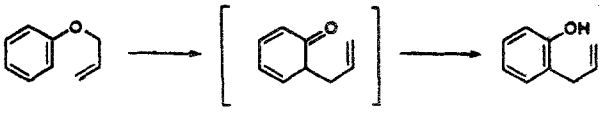
The review is devoted to literature information on the mechanism of the thio-Claisen rearrangement of allyl aryl (heteryl) sulfides and their use in the synthesis of five- and six-membered sulfur-containing heterocyclic compounds, including derivatives of dihydrobenzothiophene and thiochromane.

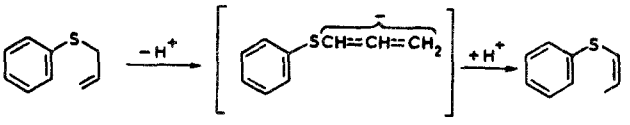
The theory of concerted reaction unites such well-known processes as the Cope and Claisen rearrangements, the 1,5-shift of a hydrogen atom in conjugated systems, etc., consisting in the migration of bonds through a cyclic transition state in which atoms or groups of atoms are added simultaneously to both ends of a π-system. Common for these rearrangements, which have been called "sigmatropic" by Woodward and Hoffman [1] is the fact that they take place in the absence of a catalyst and are initiated by the action of heat or light.

A well-known reaction of this type is the [3,3]-sigmatropic rearrangement of allyl aryl ethers, which has acquired the name of the Claisen rearrangement [2]:

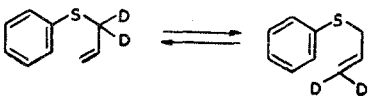


However, while the rearrangement of allyl arylethers takes place on their simple heating or in the presence of an inert solvent [3] and is a preparative method for synthesizing 2-allylphenols, the analogous reaction of allyl phenyl sulfides (thio-Claisen rearrangement) takes place only in the presence of substances of basic or acidic nature and is accompanied by a number of side reactions:

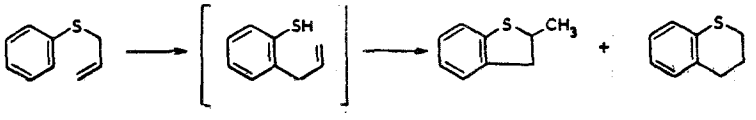
a) prototropic displacement of the double bond [4, 5]:



b) 1,3-thioallyl rearrangement [6]:



c) cyclization of the extremely unstable rearrangement products, 2-allylthiophenols, leading at the moment of their formation to 2,3-dihydrobenzothiophenes and thiochromanes [7]:



Such a complex scheme of transformations of allyl phenyl sulfides makes it difficult to study the thio-Claisen rearrangement and to interpret results on its mechanism.

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In the present review an attempt has been made to generalize literature information on the study of the mechanism of the thio-Claisen rearrangement of allyl phenyl and allyl heteryl sulfides and its use in the synthesis of sulfur-containing heterocyclic compounds. Investigations devoted to those cases of the thio-Claisen rearrangement as a result of which no formation of cyclic systems containing sulfur atoms takes place are not included in the present review, since they have been considered fairly fully in review papers on the Claisen rearrangement that have recently been published [8, 9].

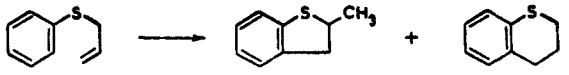
The potential possibilities of thio-Claisen rearrangement are fairly wide, since by its means it is possible to obtain various cyclic sulfides, including those modelling compounds found in mineral oils. The preparative value of this reaction is also enhanced by the fact that at the present time there are methods which permit dihydrobenzothiophenes and thiochromanes to be converted into compounds of the benzothiophene series [10, 11] and thiopyrylium salts [12] with high yields.

In contrast to the allyl aryl ethers, the allyl phenyl sulfides do not, as a rule, undergo a thermal rearrangement with the formation of the isomeric allyl thiophenols. Because of the lower energy of the C—S bond (67 kcal/mole) as compared with the C—O bond (90 kcal/mole) [13], the destruction of an allyl phenyl sulfide at the C—S bond is facilitated, and the presence of vacant d-orbitals in the sulfur atom favors the migration of the double bond in the allyl group.

On being heated in the absence of a solvent, allyl phenyl sulfide is converted only into propenyl phenyl sulfide, which readily polymerizes [4, 5]. Heating β- and γ-methylallyl phenyl sulfides [14, 15] leads to a complex mixture of products formed as the result of a prototropic displacement and reduction of the double bond, and also of the destruction of the initial solvents with the cleavage of the C—S bond.

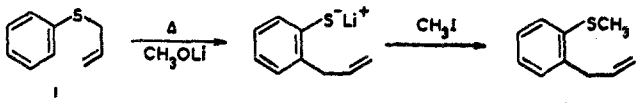
The first example of the thio-Claisen rearrangement may be considered to be the results of Petrupoulos et al. [14] on the thermal rearrangements of the S-crotyl ether of thiosalicylic acid, among the products of which 2-ethyl-2,3-dihydrobenzothiophene-4-carboxylic acid and 2-ethyl-2,3-dihydrobenzothiophene were found. The authors' assumption that the rearrangement took place with the simultaneous elimination of carbon dioxide is a fairly logical one, since it was shown by special experiments that 2-ethyl-2,3-dihydrobenzothiophene-4-carboxylic acid does not decarboxylate to 2-ethyl-2,3-dihydrobenzothiophene [14].

The first thio-Claisen rearrangement of the simplest allyl phenyl sulfide was observed by Kwart and Hacket [16]. In the products of the distillation of allyl phenyl sulfide at atmospheric pressure in the presence of quinoline and N,N-dimethylaniline, together with propenyl phenyl sulfide they found 15-20% of 2-methyl-2,3-dihydrobenzothiophene. When they repeated this work another cyclic compound — thiochromane was found among the reaction products:

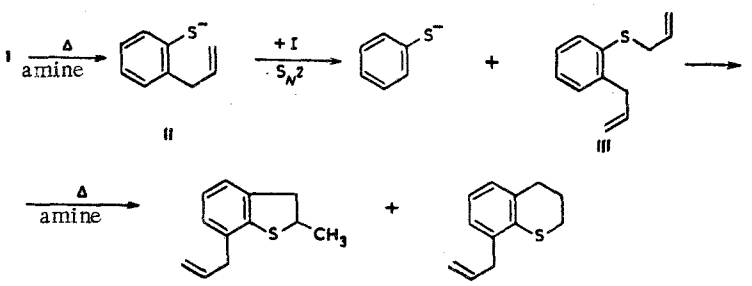


The structures of the cyclization products and also the later synthesis by Kwart of a number of substances which he considered as intermediates shows that the formation of 2-methyl-2,3-dihydrobenzothiophene and of thiochromane is possible by the cyclization of 2-allylthiophenol — the initial product of the thio-Claisen rearrangement of ally phenyl sulfide. However, in view of the pronounced tendency of 2-allylthiophenol to undergo cyclization, it was impossible to isolate it from the transformation products of allyl phenyl sulfide [7].

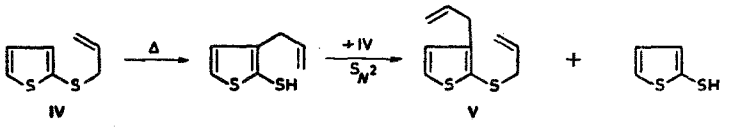
The first attempt to show the possibility that 2-allylthiophenol is an intermediate in the formation of cyclic sulfides from allyl phenyl sulfides was Kwart's study of the reactivity of 2-allylthiophenol synthesized independently [18]. It was found that 2-allylthiophenol readily cyclizes with the formation of the same cyclic compounds as in the rearrangement of allyl phenyl sulfide: at room temperature this gave 2-methyl-2,3-dihydrobenzothiophene, and on heating with quinoline it gave a mixture of 2-methyl-2,3-dihydrobenzothiophene and thiochromane [18]. Another proof of the formation of 2-allylthiophenol in the thio-Claisen rearrangement may be considered results obtained in an investigation of the transformations of allyl phenyl sulfide in quinoline in the presence of lithium methanolate [7]. In this case methyl 2-allylphenyl sulfide was obtained when the reaction mixture was treated with methyl iodide:



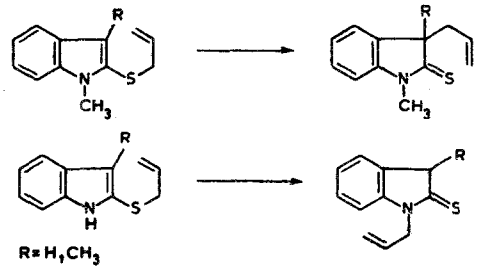
In the same investigation the formation of three compounds each containing an allyl group in a benzene ring which were the products of a successive-parallel reaction of transallylation having no analogies in the Claisen rearrangement of allyl aryl ethers was observed:



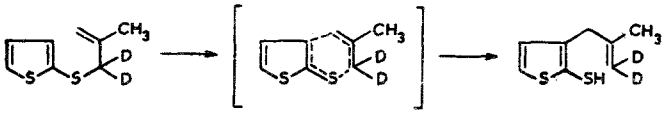
A similar course of the reaction is observed in the rearrangement of allyl thienyl sulfides (IV), but the allyl 3-allyl-2-thienyl sulfide (V) formed, unlike compound (III), does not undergo a [3,3]-sigmatropic rearrangement [19].



In contrast to allyl phenyl sulfides in the reaction products of which allyl thiophenols can be detected only by isolating their S-methyl derivatives, in the rearrangements of allyl heteryl sulfides the thiols can be isolated in the individual state [19-21]. In a number of cases, as for example, in the transformations of some allyl and propargyl indolin-2-yl sulfides [22], the rearrangement products are the corresponding thiones:



The structures of the thiols formed in the thio-Claisen rearrangement of allyl thienyl sulfides and of allyl furyl sulfides [23] unambiguously show that this reaction takes place with inversion of the allyl group through a six-membered transition state:



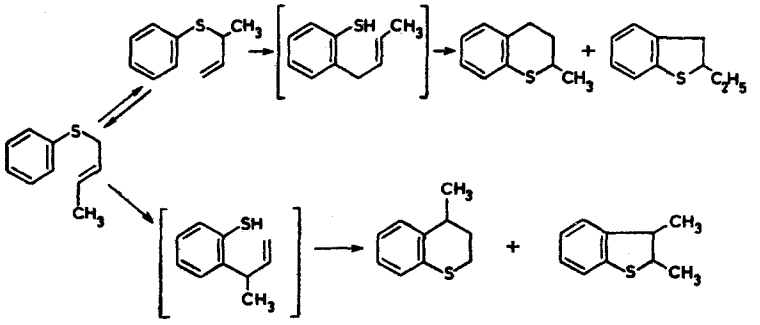
Complete inversion of the allyl group has also been shown for the case of the rearrangement of 2-(1,1-dideuteroallylthio)benzothiazole [24].

The observation of inversion of the allyl group in the rearrangement of γ-methylallyl phenyl sulfide is difficult because of the 1,3-thioallyl rearrangement taking place as a side reaction and, probably, having a lower activation energy than the thio-Claisen rearrangement and proceeding by both monomolecular and bimolecular mechanisms [6, 25]. The complex mixture of cyclic sulfides formed in the rearrangements of γ-methylallyl phenyl sulfide [26, 27] arises in the cyclization of 2-(α-methylallyl)thiophenol (inversion of the

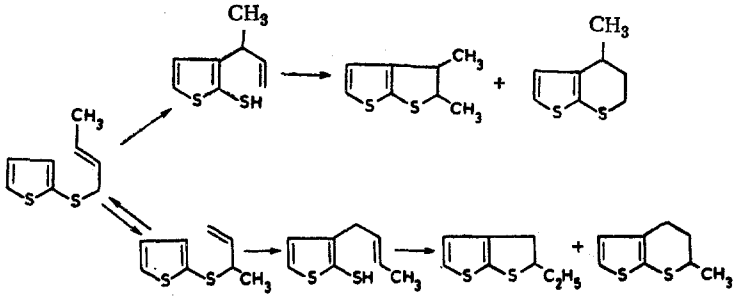
TABLE 1. Initial Rate Constants of the Rearrangement of 2-Allylthiobenzothiazole at 170°C [24]

Solvent	Isooctane	THF	Acetone	CH_3CN	i-C_8H_7OH	Carbitol	Ethanol
$k \cdot 10^4$, min^{-1}	6,177	11,84	12,04	16,31	11,56	16,50	16,38

radical in γ-methylallyl phenyl sulfide) and of 2-(γ-methylallyl)thiophenol (inversion of the radical in α-methylallyl phenyl sulfide, the product of the 1,3-thioallyl rearrangement of γ-methylallyl phenyl sulfide):



Heterocycles of analogous structure are also formed in the rearrangement of α- and γ-methylallyl thienyl sulfides [21, 28], which is also connected with the 1,3-migration of the thienyl group in the initial sulfide and with the inversion of the alkyl group on the formation of thiols from them.



Kinetic investigations of the transformations of allyl phenyl sulfides [7], of allyl thienyl and allyl furyl sulfides [23], and also of allylthiobenzothiazole [24] have shown that the thio-Claisen rearrangement is a first-order reaction the activation energy of which for allyl thienyl sulfides amounts to 13.4-24.7 kcal/mole, for γ-methylallyl furyl sulfide to 22.6 kcal/mole, and for 2-allylthiobenzothiazole to 30.4 kcal/mole. The high value of the negative entropy of activation for the transformation of 2-allylthiobenzothiazole [24] ($\Delta S^{\neq}$ = −13.4 cal/mole·deg at 170°C) shows a high symmetry of the transition state of the thio-Claisen rearrangement.

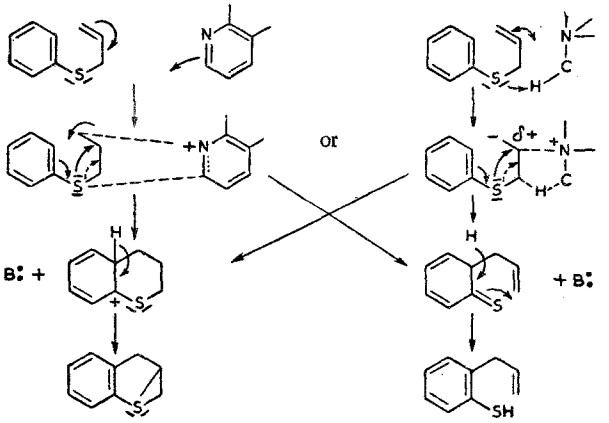
The rate of the thio-Claisen rearrangement is affected by the nature of the solvent used: In acetonitrile and acetone it is higher than in the less polar isooctane (Table 1), which shows some separation of the charges in the cyclic transition state [23, 24]. A comparison of the rate constants of the rearrangement of 2-allylthiobenzothiazole and 2-allythiobenzoxazole ($1.66 \cdot 10^3$ and $6.45 \cdot 10^{-3}$ min^{-1}) [24], and also of γ-methylallyl 2-thienyl sulfide and γ-methylallyl 2-furyl sulfide ($1.10 \cdot 10^4$ and $4.39 \cdot 10^4$ sec^{-1} at 128°C) shows that the rate of rearrangement increases with a decrease in the aromaticity of the sulfide and, consequently, is determined by the mobility of the π-electrons of a C—C bond present in the aromatic fragment of its molecule.

The unambiguous assignment of the thio-Claisen rearrangement to the class of noncatalytic concerted [3,3]-sigmatropic rearrangements can be made on the basis of information obtained by Viktorova et al. [19, 29] for allyl thienyl and allyl furyl sulfides. These sul-

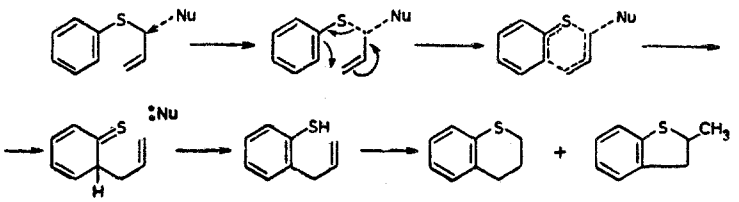
fides rearrange into the isomeric allylthiophenethiols and allylfuranthiols on simple heating in the absence of a solvent in the range of temperatures of 70-150°C.

Some known cases of rearrangements considered by the authors as purely thermal apparently cannot be considered as such, since for such compounds as quinolinyl allyl sulfides [30-33], 2-allylthiobenzothiazole [24], and indolyl allyl sulfides [20, 22] the role of a nitrogen base showing catalytic activity may be played by the substrate itself.

In the opinion of Kwart, the redistribution of electron density in amine-sulfide complexes favors the production of possible intermediates of the thio-Claisen rearrangement — a thiiranium anion or 2-allylthiophenol [15]:



However, the ideas of the formation of a thiiranium anion as an intermediate were not subsequently confirmed. On the basis of the experimental results obtained, Kwart put forward the following mechanism for the rarrangement of allyl phenyl sulfides:

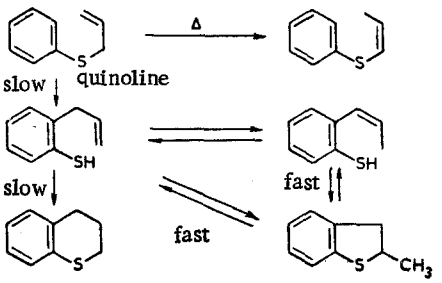


In this mechanism the participation of the amine reduces to the nucleophilic assistance in the cleavage of the C—S bond in the molecule of the initial sulfide when, in contrast to allyl aryl ethers, because of the very small difference in the electronegativities of the carbon and sulfur atoms, no displacement of electrons to the heteroatom is observed [7]. At the same time, Kwart also reports some capacity of the amine for causing a displacement of the double bond in the allyl group with the formation of propenyl phenyl sulfide.

On comparing the rates of rearrangement of allyl phenyl sulfide and 1,3-dimethylallyl phenyl sulfide ($3.40 \cdot 10^{-5}$ and $1.65 \cdot 10^{-5}$ min^{-1} at 227.8°C), Kwart came to the conclusion [7], that the presence of a methyl group on the α-carbon atom in the allyl group exerts steric hindrance to the action of the nucleophile, and on this basis he considered the most likely position of the nucleophilic attack of the sulfide by the amine molecule to be the allyl carbon atom.

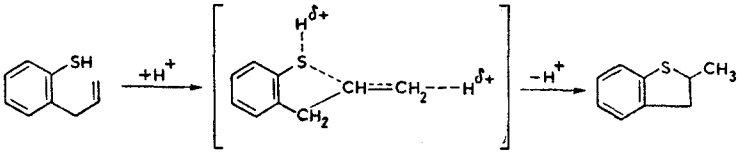
The thio-Claisen rearrangement is one of the most convenient methods of obtaining cyclic sulfides, but in the majority of cases the reaction takes place with low selectivity. Since the formation of cyclization products is observed even in the transformations of the initial allyl aryl (heteryl) sulfides, it is natural that the question of their formation is directly connected with the question of the mechanism of the thio-Claisen rearrangement.

The following scheme of the formation of 2-methyl-2,3-dihydrobenzothiophene and thiochromane in the rearrangement of allyl phenyl sulfide has been suggested [17]:

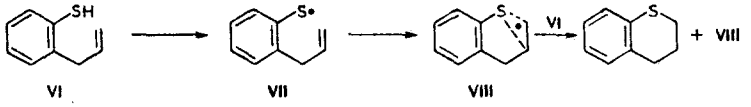


The absence of mutual isomerization of thiochromane and 2-methyl-2,3-dihydrobenzothiophene has been shown by special experiments [18], and this refutes the possibility of the thermal decyclization of the latter to 2-allylthiophenol. When 2-allylthiophenol was heated in quinoline from room temperature to 230°C, 2-methyl-2,3-dihydrobenzothiophene and thiochromane were formed in a ratio of 1:4 [18]. On the addition of 2-allylthiophenol to boiling quinoline [7], this ratio changed to 6:7, and at 300°C it proved to be 7:4.4. Thus, the cyclization of 2-allylthiophenol takes place differently according to the experimental conditions.

Kwart [7, 18] considers that the formation of 2-methyl-2,3-dihydrobenzothiophene is the result of acid catalysis through the intrinsically high acidity of 2-allylthiophenol. In actual fact, the acidity of thiophenol (pK_a 6.5) [34] considerably exceeds the acidity of phenol (pK_a 10) [35], and this ratio must obviously be preserved also for compounds with an allyl group in the ortho position with respect to SH and OH groups:

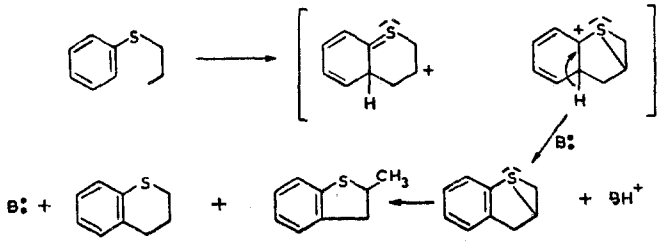


The presence of a base (quinoline) decreases the acidity of the medium and, in this case, in the opinion of Kwart and Evans [18], the reaction takes place predominantly by a radical mechanism, these authors assuming the possibility of the stabilization of the transition state through the formation of a bridge radical (VIII)



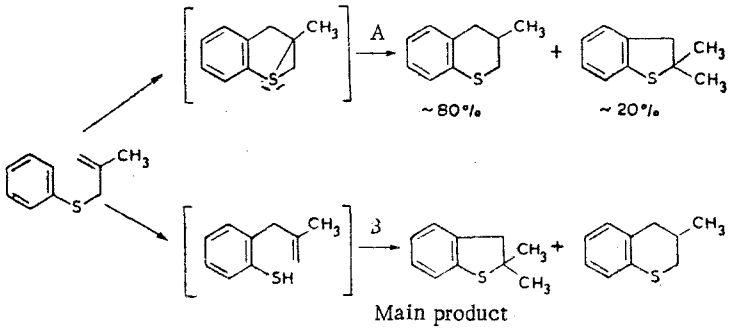
The predominant formation of thiochromane in quinoline is connected by Kwart with the higher rate of the radical process in the presence of amines as compared with the rate of the reaction in the absence of a solvent.

Since the ratio of the cyclic sulfides formed from 2-allylthiobenzothiazole [24], and that in the rearrangement of allyl phenyl sulfide (~1 : 1) the formation of both isomers from a single thiiranium ion (IX) has been suggested [18]:



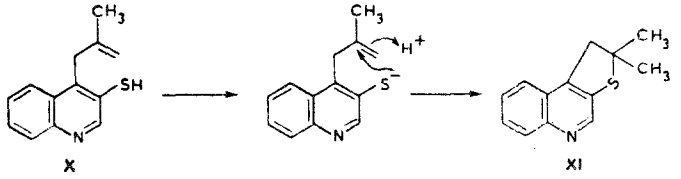
On the basis of results obtained by the authors, it would be necessary either completely to reject one of the suggested schemes of the formation of cyclic sulfides (direct cyclization through the intermediate formation of a thiiranium anion or cyclization of 2-allylthiophenol formed as an intermediate) or to recognize the simultaneous occurrence of both processes. In any case, the conclusions that they drew make the question of whether the transformation of allyl phenyl sulfides can be regarded as a thio-Claisen rearrangement a disputable one.

While for the rearrangement of allyl phenyl sulfide in quinoline a change in the temperature from 217 to 300°C does not lead to an appreciable change in the ratio of the cyclic sulfides, for β-methylallyl phenyl sulfides [15] the ratio of 2,2-dimethyl-2,3-dihydrobenzothiophene to 3-methylthiochromane changes from 1:10 at 150°C to 1:2 at 300°C. In this case it is assumed [15] that the two sulfides are formed from two different intermediate compounds — a thiiranium anion and 2-(β-methylallyl)thiophenol, with different activation energies for each of the intermediates:

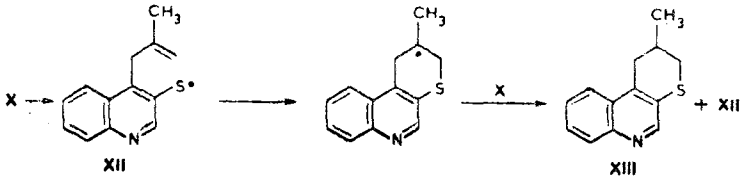


In the opinion of Kwart and Cohen [15], process A takes place with the predominant formation of 3-methylthiochromane because of the considerable strain in the five-membered ring of 2,2-dimethyl-2,3-dihydrobenzothiophene created by the two geminal methyl groups.

The cyclization of 4-(β-methylallyl)quinoline-3-thiol (X) has been studied under various conditions [31]. It was shown that the ratio of the products of the cyclization of 4-methylallylquinoline-3-thiol was identical with the isomeric composition of the cyclic sulfides formed by the rearrangement of β-methylallyl quinoline-3-yl sulfide. With a rise in the temperature from 100 to 200°C the ratio of the isomers with five- and six-membered sulfur-containing rings changed from 1 : 0.4 to 1 : 2.1, respectively. Makisumi and Murabayshi [33] have suggested an ionic mechanism of the formation of 2,2-dimethyl-2,3-dihydrothieno[3, 4-c]-quinoline (XI), including the dissociation of the thiol groups:



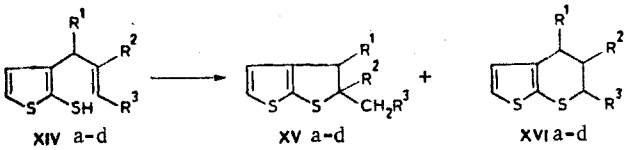
In their opinion, 3-methyldihydrothiopyrano[3,4-c]quinoline (XIII) is the product of a chain radical process:



A confirmation of this reaction scheme is the increase in the amount of the sulfide (XIII) when the reaction is carried out in the air or in the presence of an initiator — benzoyl peroxide. The signal in the ESR spectrum observed by these authors [33] during the cyclization of 3-(β-methylallyl)quinoline-4-thiol in the air is not an argument in favor of a radical process, since, in the first place, it was not determined to what concrete radical this signal could be ascribed and, in the second place, the authors did not establish the formation of a disulfide as the result of the doubling of thiyl radicals, as is always observed both in the oxidation of thiols by air [36, 37] and in the oxidative addition of thiols to olefins [38, 39]. It is also interesting to mention that a rise in the temperature had directly opposite effects on the cyclization of 2-(β-methylallyl)thiophenol [15] and 3-(β-methylallyl)quinoline-4-thiol [33]. In the first case, with a rise in the temperature

the relative amount of the five-membered isomer increased, and in the second case the relative amount of the six-membered isomer increased. Unfortunately, the information available in the literature is insufficient to explain this interesting phenomenon.

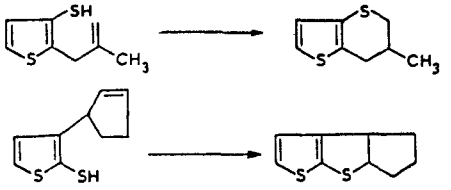
To interpret the results obtained in the cyclization of allylthiophenethiol Anisimov et al. [28] have made use of Baldwin's rules, which have a stereochemical nature [40]. The predominant cyclization of thiols (XIVa-d) into the dihydrothienothiophenes (XVa-d) or dihydrothiopyrans (XVIa-d) is connected by the authors with the possibility of the achievement in each case of a transition-state geometry favorable for the formation of compounds (XV) or (XVI).



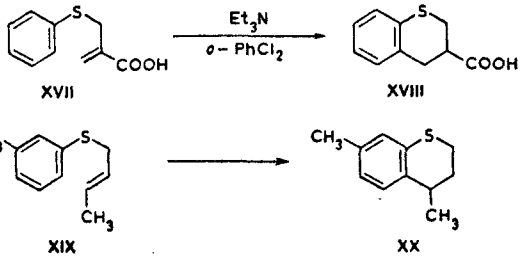
XIV a-d XV a-d XVI a-d

XIV–XVI a $R^1=R^2=R^3=H$; b $R^1=R^3=H$, $R^2=Me$; c $R^1=Me$, $R^2=R^3=H$; d $R^1=R^2=H$, $R^3=Me$

In some cases it has been possible to achieve 100% selectivity of the formation of dihydrothienothiophenes or dihydrothiopyrans [28, 41]:



The possibility of the selective formation of only one sulfide has also been observed in a study of the rearrangement of (phenylthio)methacrylic acid (XVII) [42] and of γ-methylallyl 3-methylphenyl sulfide (XIX) [18], from the transformation products of which 4,7-dimethylthiochromane (XX) was isolated with a yield of 82%:

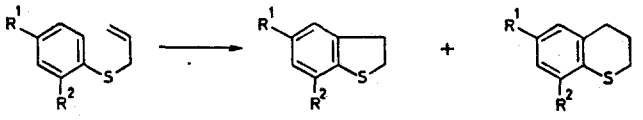


XVII XVIII

XIX XX

In those cases where several cyclic sulfides are formed as the result of the reaction, individual compounds have been isolated by using distillation [43] and preparative GLC [21]. Thus, the rearrangement of γ-methylallyl phenyl sulfide may serve as a convenient preparative method for obtaining 2-ethyl-2,3-dihydrobenzothiophene [12], and the rearrangement of allylphenyl sulfide in quinoline for obtaining 2-methyl-2,3-dihydrobenzothiophene and thiochromane [18, 43].

The rearrangement of the o- and p-tolyl allyl sulfides in quinoline has been used to obtain 2,5- and 2,7-dimethyl-2,3-dihydrobenzothiophenes and 6- and 8-methylthiochromanes, respectively [44]:

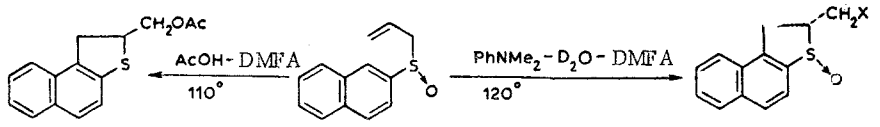


$R^1=H$, $R^2=Me$; $R^1=Me$, $R^2=H$

An interesting example of the use of thio-Claisen rearrangement in organic synthesis is provided by rearrangements [45] of aryl 2-chloroprop-2-enyl sulfides, from which 2-methylbenzothiophenes were obtained with yields of up to 80%:

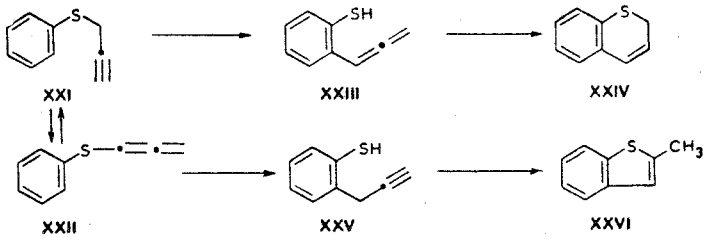
X = H, *p*-Cl, *p*-Me, *o*-Cl, *p*-OMe

The formation of sulfur-containing heterocyclic compounds has also been reported in the transformations of allyl β-naphthyl sulfoxide [46]:



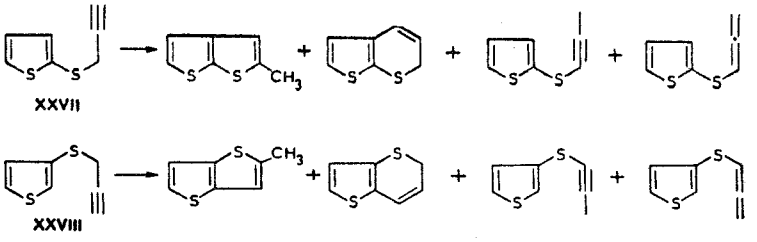
X = H, D

Reactions analogous to those that take place in the thermal and catalytic transformations of allyl phenyl sulfides also occur in the rearrangements of compounds with triple bonds under similar conditions. Thus, in quinoline at 200°C prop-2-ynyl phenyl sulfide (XXI) is converted into 2-methylbenzothiophene (XXVI) and phenyl allenyl sulfide (XXII), and in some cases (with heating above 250°C for considerable times) 2H-thiochromane (XXIV) has also been detected [47]:

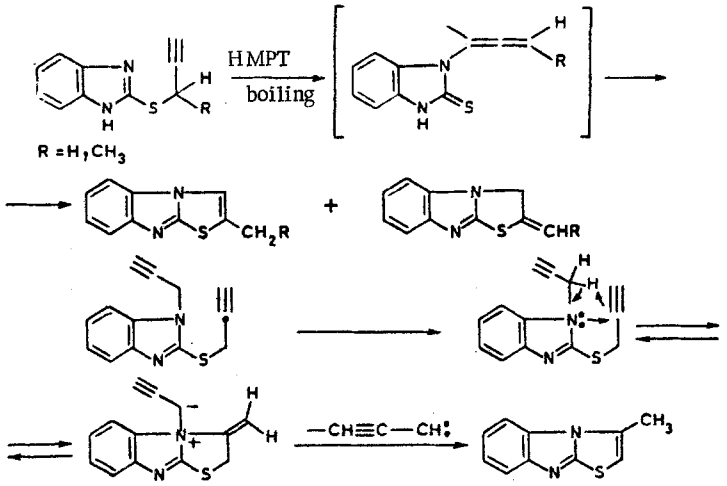


A proof of the existence of allenyl phenyl sulfide as an intermediate compound that is also subject to the thio-Claisen rearrangement has been obtained by isolating its adduct with cyclopentadiene [47]. The formation of allenyl phenyl sulfide is, as correctly assumed by the authors concerned, the result of a prototropic shift with the participation of the sulfur atom, the equilibrium XXI⇄XXII apparently being established in the reaction medium. It must be mentioned that the authors give no direct proofs of the existence of the intermediates (XXIII) and (XXV).

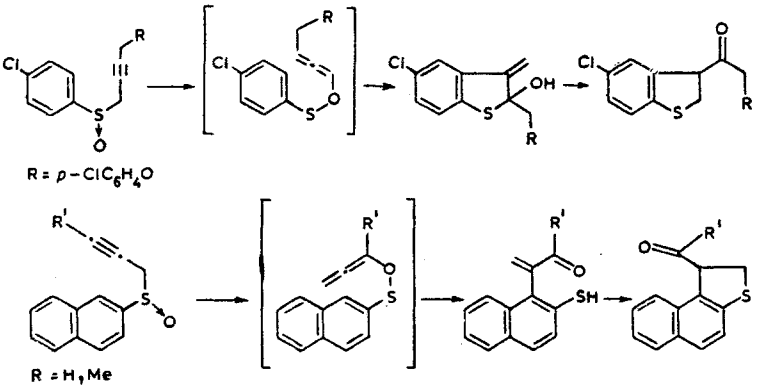
In hexamethylphosphorotriamide and dimethyl sulfoxide at 170-180°C, both 2- and 3-(propargylthio)thiophenes (XXVII) and (XXVIII) undergo a transformation of the thio-Claisen rearrangement type, forming compounds of the thienothiopyran series with good yields [48]. When rearrangement was carried out with the addition of catalytic amounts of secondary and tertiary amines [49, 50] it was established that the sulfides (XXVII) and (XVIII) formed in addition to thienothiopyrans — thienothiophenes, and also allenyl thienyl sulfides and propynyl thienyl sulfides, which are products of the prototropic displacement of the triple bond:



The rearrangement of (propargylthio)benzimidazoles leads to the formation of tricyclic compounds [51]:

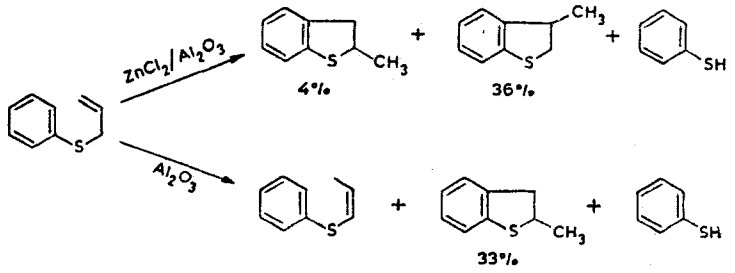


The possibility of the formation of dihydrobenzothiophene derivatives has also been reported in the transformations of aryl propynyl and arylpropargyl sulfoxides [52, 53]:



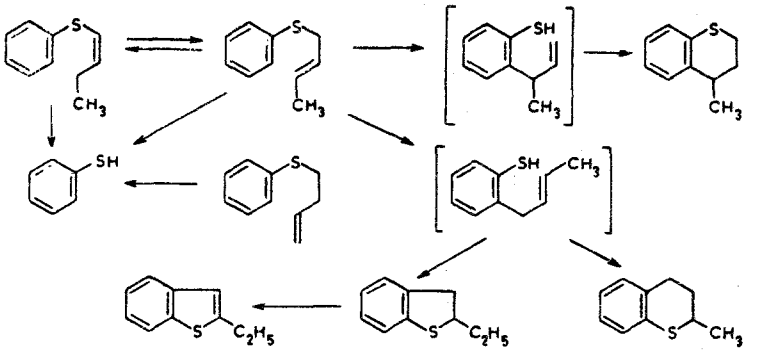
The first stage of the reaction is a [2,3]-sigmatropic rearrangement of the initial sulfoxide into an unstable allene derivation containing an S—O bond which then undergoes a [3,3]-sigmatropic rearrangement into a dihydrobenzothiophene derivative.

Transformations of alkenyl phenyl sulfides, also under conditions of heterogeneous catalysis and mainly on catalysts of acidic nature, may also be sources of cyclic sulfides. The behavior of allyl phenyl sulfide on alumina and on alumina promoted with zinc chloride has been studied [54]; the first of these catalysts possesses only Lewis acid centers [55], while the second possesses both protonic and aprotic acid centers [56]. At the same temperature (300°C) and at the same depth of conversion, reactions of allyl phenyl sulfide took place differently on the catalysts with different acidities [54]. On the catalysts with a greater acidity ($ZnCl_2/Al_2O_3$) the initial sulfide underwent cleavage to thiophenol and the formation of the isomeric 2- and 3-methyl-2,3-dihydrobenzothiophenes. On the catalyst with the lower (Al_2O_3) a prototropic isomerization into propenyl phenyl sulfide and the formation of 2-methyl-2,3-dihydrobenzothiophene was observed, while the cleavage of the C—S bond to thiophenol took place to only a very small degree:



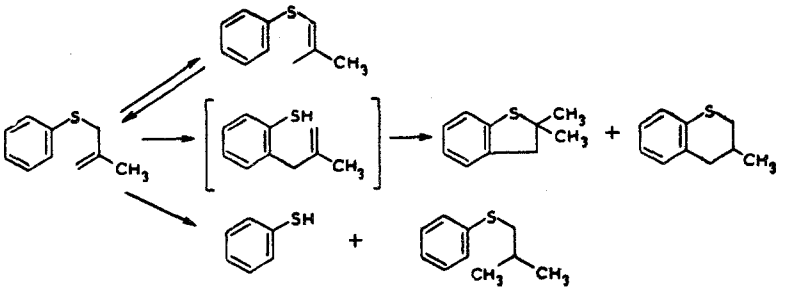
The formation of 3-methyl-2,3-dihydrobenzothiophene takes place, in the opinion of the authors concerned [54], as the result of the cyclization of the isopropenyl phenyl sulfide, which has been detected in experiments carried out at a lower temperature (200°C). It was shown by special experiments [54] that propenyl phenyl sulfide is not converted into 2-methyl-2,3-dihydrobenzothiophene under the conditions of the experiments with allyl phenyl sulfide. This gave grounds for concluding that the thio-Claisen rearrangement is the only route to the formation of 2-methyl-2,3-dihydrobenzothiophene. As was later shown by the same authors [57], the reaction products obtained in the transformations of allyl phenyl sulfide on $ZnCl_2/Al_2O_3$ contain 2- and 3-methylbenzothiophenes — the products of the dehydrogenation of the corresponding 2,3-dihydrobenzothiophenes [10]. The absence of thiochromane from the products of the transformations of allyl phenyl sulfide on acid catalysts agrees well with the results of the thermal cyclization of 2-allylthiophenol [18] and is evidence in favor of its intermediate formation in this case.

Crotyl phenyl sulfide is converted on the same catalysts (Al_2O_3 and $ZnCl_2/Al_2O_3$) [58] into 2-ethyl-2,3-dihydrobenzothiophene and 2- and 4-methylthiochromanes, and simultaneously undergoes isomerization to but-1-enyl and but-3-enyl phenyl sulfides:



The composition of the mixture of cyclic sulfides permits us to consider [58] that they are formed in the cyclization of the corresponding thiols and not by the direct cyclization of crotyl phenyl sulfide. A considerable influence on the nature of the transformations of crotyl phenyl sulfide is exerted by the acidity of the catalyst used. Thus, in the presence of Al_2O_3 it mostly isomerizes to but-1-enyl phenyl sulfide. With an increase in the acidity of the catalyst [58], in the first place the competing process of the cleavage of the initial sulfide to thiophenol is intensified and, in the second place, the composition of the cyclization products changes. The 4-methylthiochromane disappears and 2-ethyl-2,3-dihydrobenzothiophene and 2-methylthiochromane are formed in almost equal amounts (in experiments on Al_2O_3, 2-ethyl-2,3-dihydrobenzothiophene predominates).

On the basis of an investigation of the composition of the reaction products and of the stagewise nature of the process, the following scheme has been put forward for the transformations of β-methylallyl phenyl sulfide on Al_2O_3 and on Al_2O_3 promoted with HCl [59]



The yield of 2,2-dimethyl-2,3-dihydrobenzothiophene in the experiments with Al_2O_3 reaches 57% with a selectivity of the process of 75%, which permits this method to be used as a preparative one [60]. The yield of the same compound obtained on heating β-methylallyl phenyl sulfide in quinoline [15] does not exceed 31%.

Thus, literature information on the thio-Claisen rearrangement of allylaryl (heteryl) sulfides shows that its products are the corresponding allylarylthiols or allylheterylthiols which, under the reaction conditions, can be converted into sulfur-containing heterocyclic compounds. A variation of the conditions of the reaction, and also of the structure of the initial sulfides, permits cyclic sulfides to be obtained with high yield and high selectivity in a number of cases.

LITERATURE CITED

1. R. B. Woodward and R. Hoffman, Angew. Chem., Int. Ed., 8, 781 (1969).
2. H. J. Hansen and H. Schmid, Chem. Brit., No. 2, 111 (1969).
3. L. Claisen, Ber., 45, 3757 (1912).
4. E. N. Karaulova, D. Sh. Meilanova, and G. D. Gal'pern, Dokl. Akad. Nauk SSSR, 113, 1280 (1957).
5. E. N. Karaulova, D. Sh. Meilanova, and G. D. Gal'pern, Zh. Obshch. Khim., 27, 3034 (1957).
6. H. Kwart and N. A. Johnson, J. Am. Chem. Soc., 99, 3441 (1977).
7. H. Kwart and J. L. Schwartz, J. Org. Chem., 39, 1575 (1974).
8. S. J. Rhoads and N. R. Raulins, Org. Reactions, 22, 1 (1975).
9. J. B. Bennet, Synthesis, No. 9, 589 (1977).
10. A. N. Korepanov, T. A. Danilova, and E. A. Viktorova, Neftekhimiya, 16, 909 (1976).
11. É. A. Karakhanov, M. V. Vagabov, E. A. Viktorova, and A. Sh. Ramazanov, Vestn. Mosk. Univ., Ser. 2, Khim., 19, 362 (1978).
12. A. V. Anisimov, L. M. Kedik, L. P. Ermolenko, and E. A. Viktorova, Neftekhimiya, 17, 148 (1977).
13. S. Oae, Organic Chemistry of Sulfur, Plenum, New York (1977).
14. J. C. Petropoulos, M. A. McCall, and D. S. Tarbell, J. Am. Chem. Soc., 75, 1130 (1953).
15. H. Kwart and M. H. Cohen, J. Org. Chem., 32, 3135 (1967).
16. H. Kwart and C. M. Hacket, J. Am. Chem. Soc., 84, 1754 (1962).
17. J. Meyers, C. Rinaldi, and J. Banoli, J. Org. Chem., 28, 2440 (1963).
18. H. Kwart and E. R. Evans, J. Org. Chem., 31, 413 (1966).
19. A. V. Anisimov, V. F. Ionova, and E. A. Viktorova, Zh. Org. Khim., 13, 2624 (1977).
20. H. Plieninger, H.-P. Kraemer, and H. Sirowej, Chem. Ber., 107, 3915 (1974).
21. J. Z. Mortensen, B. Hedegaard, and S.-O. Lawesson, Tetrahedron, 27, 3832 (1971).
22. B. W. Bicroft and W. Landon, Chem. Commun., No. 3, 168 (1970).
23. A. V. Anisimov, V. F. Ionova, V. K. Govorek, V. S. Babaitsev, and E. A. Viktorova, Dokl. Akad. Nauk SSSR, 244, 362 (1979).
24. T. Takahashi, A. Kaji, and Yun-ichi-Hayami, Bull. Inst. Chem. Res. Kyoto Univ., 51, 163 (1973).
25. H. Kwart and N. A. Johnson, J. Am. Chem. Soc., 92, 6064 (1970).
26. H. Kwart and N. H. Cohen, Chem. Commun., No. 6, 319 (1968).
27. T. A. Danilova, L. V. Sitnikova, T. Abdin, and E. A. Viktorova, Vestn. Mosk. Univ., Ser. 2, Khim., 17, 591 (1976).
28. A. V. Anisimov, V. F. Ionova, V. S. Babaitsev, V. K. Govorek, and E. A. Viktorova, Khim. Geterotsikl. Soedin., No. 8, 1062 (1979).
29. A. V. Anisimov, V. F. Ionova, and E. A. Viktorova, Vestn. Mosk. Univ. Ser. 2, Khim., 19, 729 (1978).
30. J. Makisumi and A. Murabayashi, Tetrahedron Lett., No. 24, 1971 (1969).
31. J. Makisumi and A. Sasatani, Tetrahedron Lett., No. 24, 1975 (1969).
32. J. Makisumi and A. Murabayshi, Tetrahedron Lett., No. 29, 2449 (1969).
33. J. Makisumi and A. Murabayashi, Tetrahedron Lett., No. 29, 2453 (1969).
34. A. Albert and E. Serjeant, Ionization Constants of Acids and Bases, Methuen, London (1962).
35. F. G. Bordwell and G. D. Copper, J. Am. Chem. Soc., 74, 1058 (1952).
36. N. Kharasch, Organic Sulfur Compounds, Pergamon, Oxford, Vol. 1 (1961), p. 97.
37. T. McAllan and T. W. Cullum, J. Am. Chem. Soc., 73, 3627 (1951).
38. A. A. Oswald and F. Noel, J. Org. Chem., 26, 3948 (1961).
39. A. A. Oswald, F. Noel, and A. J. Stephenson, J. Org. Chem., 26, 3969 (1961).
40. J. F. Baldwin, Chem. Commun., No. 18, 734 (1976).
41. A. V. Anisimov, V. F. Ionova, V. S. Babaitsev, and E. A. Viktorova, Zh. Org. Khim., 15, 882 (1979).
42. B. Gopalan, K. Rajagopalan, S. Swaminatham, and K. K. Balasubramanian, Synthesis, No. 4, 409 (1976).

43. S. Khushvakhtova, A. N. Korepanov, T. A. Danilova, and E. A. Viktorova, Vestn. Mosk. Univ. Ser. 2, Khim., 13, 574 (1972).
44. E. N. Karaulova, G. D. Gal'pern, V. D. Nikitina, and I. V. Cherepanova, Neftekhimiya, 7, 774 (1967).
45. W. K. Anderson, E. J. LaVoic, and J. C. Battaro, J. Chem. Soc. Perkin Trans. I, No. 1, 1 (1976).
46. Y. Makisumi, S. Takada, and Y. Matsukara, Chem. Commun., No. 20, 850 (1974).
47. H. Kwart and T. J. George, Chem. Commun., No. 7, 433 (1970).
48. L. Brandsma and H. J. Bos, Rec. Trav. Chim., 88, 732 (1969).
49. L. Brandsma and D. Shuijl-Laros, Rec. Trav. Chim., 89, 110 (1970).
50. L. Brandsma, P. J. W. Schuijl, D. Schuijl-Laros, J. Mejer, and H. E. Wijers, Int. J. Sulfur Chem., 68, 85 (1971).
51. K. K. Balasubramanian and B. Venugopalan, Tetrahedron Lett., No. 31, 2643, 2645 (1974).
52. K. C. Majumdar and B. S. Thyagarajan, Chem. Commun., No. 2, 83 (1972).
53. Y. Makisumi and S. Takada, Chem. Commun., No. 20, 848 (1974).
54. S. Khushvakhtova, E. A. Viktorova, and T. A. Danilova, Vestn. Mosk. Univ., Ser. 2, Khim., 10, 99 (1969).
55. A. E. Perry, J. Phys. Chem., 69, 211 (1965).
56. E. A. Karakhanov, V. P. Galkin, A. V. Anisimov, A. G. Debov, and E. A. Viktorova, Zh. Fiz. Khim., 41, 977 (1977).
57. S. Khushvakhtova, E. A. Viktorova, and T. A. Danilova, Vestn. Mosk. Univ., Ser. 2, Khim., 14, 97 (1973).
58. T. Abdin, T. A. Danilova, and E. A. Viktorova, Khim. Geterotsikl. Soedin., No. 10, 1337 (1973).
59. G. Dzhamalova, T. A. Danilova, and E. A. Viktorova, Zh. Org. Khim., 12, 76 (1976).
60. A. N. Korepanov, T. A. Danilova, E. A. Viktorova, and L. M. Sladkova, Vestn. Mosk. Univ., Ser. 2, Khim., 14, 379 (1973).