REARRANGEMENT OF ALLYL THIENYL SULFIDES TO ALLYLTHIOPHENETHIOLS

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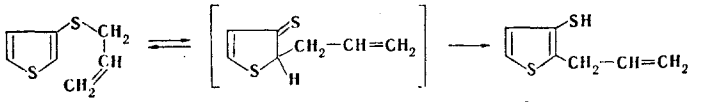
It is shown that the rearrangement of allyl 2-thienyl and allyl 3-thienyl sulfides in various solvents at 89-136°C gives the corresponding allylthiophenethiols, which can subsequently undergo transallylation with the starting sulfide and cyclization to thienodihydrothiopyrans and methyldihydrothienothiophenes. The energy of activation of the rearrangement of both isomeric sulfides is 19 kcal/mole. The pK_a values of thiophenyl and some thiols of the thiophene series were determined, and it was established that the acidities of the allylthiophenethiols do not have a decisive effect on their ability to undergo cyclization.

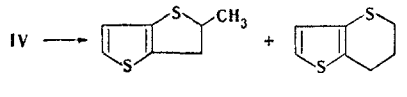
The final products in the 3,3-sigmatropic rearrangement of allyl thienyl sulfides are compounds of the thienodihydrothiopyran and 2,3-dihydrothienothiophene series [1], which, as in the case of the rearrangement of allyl phenyl sulfide, are formed by cyclization of the corresponding thiols — the primary products of the rearrangement of sulfides. However, up until now the problems involved in the formation and reactivities of aromatic allyl thiols have not been adequately illuminated in the literature.

We detected the corresponding 3-allylthiophene-2-thiol (III) and 2-allylthiophene-3-thiol (IV) in the products of the rearrangement of allyl 2-thienyl (I) and allyl 3-thienyl (II) sulfides in various solvents (amines, carboxylic acids, and hydrocarbons); the yields of III and IV varied as a function of the temperature, the reaction time, and the nature of the solvent. For example:

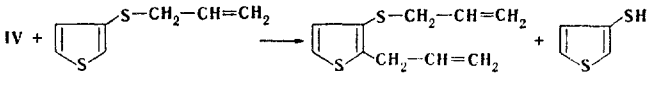


II IV

Thus the yield of thiol III increased from 6 to 66% in the rearrangement in m-xylene for 2 h as the temperature changed from 89 to 136°C, as compared with 8 and 32%, respectively, for thiol IV. The yields of thiols in the case of reaction in N,N-dimethylaniline did not exceed 26% under the optimum conditions (118°C for 2 h); this is associated with competitive cyclization and transallylation reactions:



V VI



II VII

The rearrangement proceeds similarly in acetic acid, but the resulting thiols undergo S acylation.

The neutral products of rearrangement of II were investigated by chromatographic mass spectrometry. Compounds V-VII were recorded in the reaction mixture. The molecular weight of V is 156, and the intensity of the $[M + 2]^+$ ion peak (~9%) provides evidence for the presence of two sulfur atoms in the molecule. The principal pathway of mass spectrometric

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fragmentation of V is the characteristic (for methyldihydrobenzothiophenes [2]) elimination of a hydrogen atom, a methyl radical, and an $SH^{\cdot}$ radical; this makes it possible to assign the 2-methyl-2,3-dihydrothieno[3,2-b]thiophene structure to V. Compound VI is an isomer of V. The $[M + 2]^+$ ion peak in the spectrum of VI has an intensity of 9% that of the molecular ion peak; the principal fragmentation pathway under the influence of electron impact is retrograde diene ejection of a C_2H_4 group; this made it possible to assign the thieno[3,2-b]dihydrothiopyran structure to VI.

Compound VII has a molecular mass of 196 and also contains two sulfur atoms. The molecular ion peak is of very low intensity, and the principal peak in the mass spectrum is the $[M - C_3H_4]^+$ ion peak, which is formed as a result of elimination of an allyl group, accompanied by migration of a hydrogen atom. The subsequent fragmentation of this fragment ion is associated with the characteristic (for sulfur-containing compounds) ejection of an SH radical. The most probable structure for VII is the allyl 3-(2-allylthienyl) sulfide structure.

Cyclization can be avoided under certain conditions in the rearrangement of I and II. By disregarding the transallylation process, we estimated the kinetic parameters of 3,3-sigmatropic rearrangement of these sulfides from the initial reaction rates, which are satisfactorily described by a first-order equation. The apparent energies of activation of 3,3-sigmatropic rearrangement of I and II were practically identical [79.5 kJ/mole (19 kcal/mole)]. These values are considerably lower than the corresponding values in the case of the Claisen rearrangement of allyl phenyl ether (132 kJ/mole (31.6 kcal/mole) [3]). The maximum error in the determination of the energy of activation of rearrangement of I and II calculated with allowance for the contribution of transallylation does not exceed 12.5 kJ/mole (3 kcal/mole) for I and 16.7 kJ/mole (4 kcal/mole) for II.

The considerably lower temperature barrier of the 3,3-sigmatropic rearrangement of I and II (89°C) as compared with allyl phenyl sulfide (k = 0 over the entire investigated temperature range) makes it possible to assume that the energy of activation for the rearrangement of allyl phenyl sulfide is also higher than the values for allyl thienyl sulfides.

It is known that 2-allylphenols are quite stable under the conditions of the Claisen rearrangement, whereas 2-allylthiophenol undergoes complete cyclization at 25°C, in connection with which it cannot be isolated in the rearrangement of allyl phenyl sulfide. Compounds III and IV are quite stable when they are heated to 100°C in xylene but undergo cyclization somewhat more readily in dimethylaniline. Since Kwart and Schwartz [4] associate the instability of 2-allylthiophenol with its high acidity, one should have compared the pK_a values of the thiols of the thiophene series with the corresponding values for 2-allylphenol and thiophene. We determined the acidity of thiophenol, since the data presented in [5-7] are contradictory: pK_a 8.3, 7.74, and 6.5, respectively.

The results of the measurements (Table 2) show that the acidities of the thiols are considerably higher than the acidities of the phenols. However, in the series of investigated thiols the pK_a values differ very little and do not explain the higher resistance of III and IV with respect to cyclization as compared with 2-allylthiophenol.

EXPERIMENTAL

The reaction products were analyzed with a Tsvet-4 chromatograph with a flame ionization detector, an SE-60 liquid phase, a Chromosorb W support (60-80 mesh), nitrogen as a carrier gas, and an analysis temperature of 150°C. Chromatographic mass spectrometry was carried out with a Varian MAT-111 (Gnom) apparatus. The PMR spectra of CCl_4 solutions of the compounds were recorded with a Varian T-60 spectrometer with hexamethyldisiloxane as the internal standard. The IR spectra of thin layers of the compounds were recorded with a UR-20 spectrometer. The UV spectra were recorded with an SF-4A spectrometer.

Allyl 2-Thienyl Sulfide (I). This compound, with bp 66-67°C (3 mm) and n_D^{20} 1.5898, was obtained by the method in [1]. PMR spectrum: 6.65-7.1 (α-H, β-H, β'-H, 3H, m), 5.4-6.0 (CH, 1H, m), 4.63-4.9 ($=CH_2$, 2H, m), and 3.16 ppm (CH_2, 2H, d).

Allyl 3-Thienyl Sulfide (II). This compound, with bp 79-80°C (4 mm) and n_D^{20} 1.5909, was obtained by the method in [10]. PMR spectrum: 6.7-7.1 (α-H, α'-H, β-H, 3H, m), 5.9-6.0 (CH, 1H, m), 4.7-5.0 ($=CH_2$, 2H, m), and 3.25 ppm (CH_2, 2H, d).

TABLE 1. Kinetic Parameters in the Rearrangement of Allyl Thienyl Sulfides

Sulfide	$k \cdot 10^3$, min^{-1}						E_a	
	89°	105°	108°	118°	128°	136°	kcal/mole	kJ/mole
I	—	5,46	—	12,2	27,4	36,7	19	79,5
II	2,2	—	8,5	14,8	—	43,7	19	79,5

TABLE 2. Acidity Constants of Thiols*

	Thiol					
	thiophenol	thiophene-2-thiol	thiophene-3-thiol	3-allylthiophene-2-thiol	2-allylthiophene-3-thiol	2-tert-butyl-4-allylthiophene-5-thiol
λ, nm	265	290	280	290	280	290
pK_a	6,7	6,7	6,8	6,9	6,9	7,0

*The pK_a of phenol [8] is 10.0 and the pK_a of 2-allylphenol [9] is 10.28.

Thiophene-3-thiol. This compound, with bp 59-60°C (12 mm) and n_D^{20} 1.6216, was obtained by the method in [11]. PMR spectrum: 6.5-6.95 (α-H, β-H, β'-H, 3H, m) and 3.25 ppm (SH, 1H, s). IR spectrum: 2530 cm^{-1} (SH).

Thiophene-2-thiol. This compound, with bp 46-48°C (5 mm) and n_D^{20} 1.6208, was obtained by the method in [12]. PMR spectrum: 6.5-6.9 (α-H, β-H, β'-H, 3H, m) and 3.3 ppm (SH, 1H, s). IR spectrum: 2530 cm^{-1} (SH).

Allyl 5-(2-tert-Butylthienyl) Sulfide. This compound, with bp 104-106°C (3 mm), was obtained by the method used to prepare I. PMR spectrum: 6.8 (1H, d) and 6.6 (1H, d), 3-H and 4-H; 5.3-5.9 (CH, 1H, m); 4.5-4.9 (=CH_2, 2H, m); 3.15 (CH_2, 2H, d); and 1.2 ppm (CH_3, 9H, s).

2-tert-Butyl-4-allylthiophene-5-thiol. This compound was obtained during distillation of the latter sulfide as a result of partial rearrangement. PMR spectrum: 6.4 (3-H, 1H, s), 5.3-5.8 (CH, 1H, m), 4.6-5.0 (=CH_2, 2H, m), 3.2 (CH_2, 2H, d), 2.9 (SH, 1H, s), and 1.2 ppm (CH_3, 9H, s). IR spectrum: 2530 cm^{-1} (H).

The rearrangement of I and II was carried out in a thermostated flask with a jacket in a stream of argon with stirring at 89-136°C.

3-Allylthiophene-2-thiol (III). This compound, with bp 68-71°C (3 mm) and n_D^{20} 1.5895, was isolated from the products of rearrangement of I. PMR spectrum: 6.96 (α-H, 1H, d), 6.66 (β-H, 1H, d), 5.45-6.10 (CH, 1H, m), 4.7-5.0 (=CH_2, 2H, m), 3.26 (CH_2, 2H, d), and 3.03 ppm (SH, 1H, s). IR spectrum (thin layer): 2532 cm^{-1} (SH).

2-Allylthiophene-3-thiol (IV). This compound, with bp 72-74°C (3 mm) and n_D^{20} 1.5885, was isolated from the product of rearrangement of sulfide II. PMR spectrum: 6.80 (β-H, 1H, d), 7.0 (α-H, 1H, d), 5.5-6.2 (CH, 1H, m), 4.8-5.2 (=CH_2, 2H, m), 3.5 (CH_2, 2H, d), and 2.9 ppm (SH, 1H, s). IR spectrum (thin layer): 2530 cm^{-1} (SH).

The acidities of the thiols were determined by UV spectroscopy. Acetate–ammonia solutions were used as buffer solutions. The constant ionic strength (0.5) was created by the addition of a solution of potassium chloride. The pK_a values were determined from the formula $pK_a = pH - \ln[(D - D_{HA})/(D_A - D)]$, where D is the optical density of the equilibrium mixture, D_{HA} is the optical density of a solution containing only the undissociated thiol molecule, and D_A is the optical density of a solution containing only the dissociated thiol molecule.

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TAUTOMERISM AND SPATIAL ISOMERISM IN THE 2-PHENYLAMINOTHIAZOLIN-4-ONE SERIES

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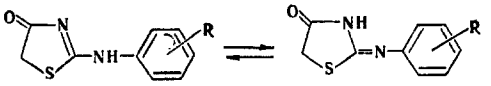
The existence of amine—imine tautomerism in 2-phenylaminothiazolin-4-ones was confirmed by comparison of the IR and UV spectra of these compounds with N-methyl model compounds with amine and imine structures. It is shown that the temperature changes in the PMR spectra are associated with syn—anti isomerization relative to the exocyclic CN bond. The kinetic parameters of this isomerization were calculated, and it was established that it is realized in the imine form via an inversion mechanism.

A pronounced dependence of the form and position of the signals of the phenyl protons on the temperature is observed in the PMR spectra of p-substituted 2-phenylaminothiazolin-4-ones (solutions in deuterodimethylformamide, deuteropyridine, and deuteroacetone). At high temperatures the signals of these protons correspond to the four-spin AA'BB' system (Fig. 1, spectrum a). As the temperature is lowered, the doublet of the ortho protons becomes broader, a coalescence stage occurs (Fig. 1, spectrum b), and the doublet is split into two doublets (Fig. 1, spectra c and d). At low temperatures the nonequivalence of the meta protons is also manifested (Fig. 1, spectrum d). For the investigated series of compounds this is also accompanied by splitting of the signals of the CH_2 group of the thiazoline ring into a doublet.

The temperature changes in the spectra indicate the existence in the investigated substances of two molecular forms in equilibrium with one another; the rate of conversion from one form to the other increases appreciably as the temperature is raised. In the case under consideration the appearance of different molecular forms may be due to tautomerism, syn—anti isomerism, or conformation isomerism due to retarded rotation of the phenyl group about the N—C_6H_5 bond.

The amine—imine tautomerism (IA—IB) of 2-arylamino derivatives of thiazolin-4-one was previously detected by means of the IR spectra [1, 2] and an examination of the dependence of the pK_a values on the σ^o values [3].

In the present research we made a more detailed study of the tautomerism of these compounds by means of model compounds (II-V):



IA IB

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