Preparation of Deuterated Products. A reaction vessel of the "duck" type was charged with 0.1-0.3 g [$(3-9)\cdot10^{-5}$ mole/Pd] of the catalyst, $(1-3)\cdot10^{-3}$ g of $NaBH_4$, and $(2-8)\cdot10^{-3}$ mole of the HBr acceptor, argon was blown through the vessel, 3-15 ml of the solvent (methanol, ethanol, or D_4-methanol with a purity of >98%) was added by syringe through the resin condensate, and the stirrer was switched on. After 15-20 min (after decomposition of the $NaBH_4$), D_2 (98-99% pure) was blown into the reactor, the mixture was heated to the necessary temperature, and a solution of $(1-4)\cdot10^{-3}$ mole of the substrate in 2-5 ml of the solvent was added. The composition of the products was studied by GLC and PMR spectroscopy. The degree of deuteration reached 95-97% and was determined by means of integral curves from the H^4 signals for 4-deutero-2-acetylthiophene (7.07 ppm in CCl_4), 4-deutero-2-formylthiophene [7.15 ppm in $(CD_3)_2CO$], 4,5-dideutero-2-formylthiophene (6.95 ppm in CD_3OD), and methyl 4,5-dideuterofuran-2-carboxylate (7.00 ppm in CD_3OD).

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[3,3]-SIGMATROPIC REARRANGEMENT OF CHLORO-SUBSTITUTED ALLYL THIENYL SULFIDES

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The kinetics of the rearrangement of allyl 5-chloro-2-thienyl sulfide and β-chloroallyl 2-thienyl sulfide to, respectively, 5-chloro-3-allyl-2-thiophenethiol and 3-(β-chloroallyl)-2-thiophenethiol were investigated. It is shown that an acceptor substituent in the allyl group decreases the reactivity of the sulfide significantly, whereas an acceptor in the heterocyclic ring does not have an appreciable effect on it.

A study of the [3,3]-sigmatropic rearrangement of allyl thienyl sulfides has shown [1] that a six-membered transition state with partial charge separation is most likely for it. In contrast to sulfides of the benzene series, stable allylthiophenethiols are the products of rearrangement of allyl thienyl sulfides.

We have studied the rearrangement of allyl 5-chloro-2-thienyl sulfide (Ia) and β-chloroallyl-2-thienyl sulfide (Ib):

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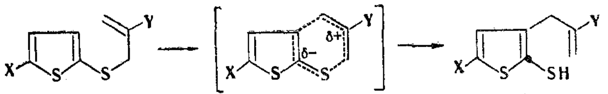

I   II

I, II a X=Cl, Y=H; b X=H, Y=Cl

A study of the kinetics of the rearrangement has shown (Table 1) that it is a first-order reaction and has a high negative entropy of activation. The polarity of the solvent has a slight effect on the rate constant of the reaction and its energy of activation; this is also characteristic for other [3,3]-sigmatropic rearrangements.

A comparison of the rate constants and the energies of activation for the rearrangement of β-chloroallyl-2-thienyl sulfide and unsubstituted allyl 2-thienyl sulfide showed that the latter undergoes rearrangement considerably more readily. An acceptor substituent, by increasing the positive charge in the allyl portion, probably reduces the aromatic character of the transition state [2]. The appreciable increase in the reaction rate in the case of the rearrangement of β-chloroallyl 2-thienyl sulfide in polar solvents, viz., dibutyl ether and hexametapol, constitutes evidence in favor of the existence of significant charge separation in the transition state.

An acceptor substituent in the thiophene ring decreases the rearrangement rate constant only slightly without affecting the energy of activation, as has been observed in the case of Claisen rearrangement in the allyl phenyl ether series [3].

EXPERIMENTAL

The PMR spectra of solutions of the compounds in CCl_4 were recorded with a Varian T-60 spectrometer with hexamethyldisiloxane as the internal standard. The IR spectra of films of the compounds were recorded with an IKS-22 spectrometer.

The experiments for the study of the kinetics of the rearrangement were carried out in thin 0.5-cm^3 ampuls in an argon atmosphere. The thiol concentration in the reaction mixture was determined every 10 min. For this, an aliquot of the reaction mixture was diluted with ethanol to a thiol concentration of $(0.2\text{-}2.0)\cdot 10^{-6}$ mole/ml, 0.1 ml of this solution was mixed with 4.9 ml of a standard solution of the reagent, viz., 2,2'-dithiobis(5-nitropyridine), and the optical density at 480 nm was measured with a Spectromom-410 spectrometer. Only 5-nitro-2-thiopyridone, which is liberated instantaneously in an equivalent amount upon reaction of the thiol with 2,2'-dithiobis(5-nitropyridine) [4], absorbs in the indicated region. A standard solution of the reagent contained 10^{-4} mole of 2,2'-dithiobis(5-nitropyridine) in 100 ml of a mixture of ethanol and a phosphate buffer (9:1). To prepare the phosphate buffer, 0.358 g of $Na_2HPO_4\cdot 12H_2O$ was dissolved in 90 ml of distilled water, the solution was adjusted to pH 5.9 by the addition of a 0.1 N solution of hydrochloric acid, and water was added to bring the total volume to 100 ml. The thiol concentration was determined from a calibration graph. The rearrangement rate constants were calculated from the initial sections of the kinetic curves, at which points the contributions of side processes are minimal.

Allyl 5-Chloro-2-thienyl Sulfide (Ia). This compound was synthesized by the general method for the synthesis of allyl hetaryl sulfides [5] by the reaction of 5-chloro-2-thiophenethiol and allyl bromide in an aqueous solution of alkali. The product was obtained in 51% yield and had bp 72-73°C (1 mm), n_D^{20} 1.5888, and d_4^{20} 1.1901. Found: C 44.3; H 3.9; S 29.1%. $C_7H_7ClS_2$. Calculated: C 44.1; H 3.7; S 33.6%. PMR spectrum: 6.7 (2H, m, C_4H_2S), 5.7 (1H, m, $-CH=$), 5.0 (2H, m, $=CH_2$), and 3.2 ppm (2H, d, CH_2).

β-Chloroallyl 2-Thienyl Sulfide (Ib). This compound was synthesized similarly from 2-thiophenethiol and 2,3-dichloropropene. The product was obtained in 60% yield and had bp 84-85°C (1 mm), n_D^{20} 1.5855, and d_4^{20} 1.2122. Found: C 44.2; H 3.8; S 32.3%. $C_7H_7ClS_2$. Calculated: C 44.1; H 3.7; S 33.6%. PMR spectrum: 7.3 (3H, m, C_4H_3S), 5.35 (1H, m, $=CH$), 5.2 (1H, m, $=CH$), and 3.65 ppm (2H, s, CH_2).

5-Chloro-3-allyl-2-thiophenethiol (IIa). This compound was obtained by rearrangement of sulfide Ia. A mixture of 1.6 g of sulfide Ia with 3 ml of m-xylene was heated in a sealed (in an argon atmosphere) ampul at 105°C for 3 h, after which it was diluted with ether, and the thiol was extracted several times with a 10% aqueous solution of sodium hydroxide. The alkaline extract was acidified with dilute hydrochloric acid, and the thiol was extracted with ether. The extract was dried with magnesium sulfate, the ether was removed by distilla-

TABLE 1. Kinetic Parameters of the Rearrangement of Sulfides

Sulfide	Solvent	Temp., °K	$k\cdot 10^4$, sec^{-1}	E_a, kcal/mole	$-\Delta S^{\neq}$, kcal/mole · deg
Allyl 2-thienyl sulfide	m-Xylene	353	0,04	19±2	31,7
		363	0,07		
		378	0,28		
		391	0,70		
Ia	m-Xylene	353	0,03	19±2	32,3
		363	0,05		
		376	0,11		
		386	0,18		
Ia	Dibutyl ether	363	0,04		
Ia	Tetrachloroethylene	363	0,06	19±2	32,5
		376	0,15		
		386	0,27		
Ib	m-Xylene	398	0,03	25±2	23,6
		413	0,08		
		428	0,20		
Ib	Dibutyl ether	413	2,00		
Ib	Hexametapol	363	0,10	25±2	14,9
		398	1,50		
		413	4,90		

tion, and the residue was distilled *in vacuo* to give 0.3 g (19%) of thiol IIa with bp 73-74°C (1 mm) and n_D^{20} 1.5915. PMR spectrum: 6.7 (1H, s, 4-H), 5.8 (1H, m, —CH=), 5.1 (2H, m, =CH$_2$), 3.35 (2H, d, CH$_2$), and 3.05 ppm (1H, s, SH). IR spectrum: 2550 (w, S—H) and 1650 cm^{-1} (m, C=C).

3-(β-Chloroallyl)-2-thiophenethiol (IIb). This compound was obtained by rearrangement of β-chloroallyl 2-thienyl sulfide (Ib) to hexametapol. A 17-ml sample of hexametapol was heated to 160°C in a flask equipped with a reflux condenser in an argon atmosphere, after which 2 g of sulfide Ib was added with stirring, and heating was continued for 30 min. The mixture was then poured into 50 ml of cold water, and 50 ml of a 20% solution of sodium hydroxide was added. Thiol IIb was isolated from the alkaline solution as in the case of IIa to give 1.3 g (65%) of a product with bp 87-89°C (1 mm) and n_D^{20} 1.5905. PMR spectrum: 7.0 (2H, m, 4-H, 5-H), 5.15 (1H, m, =CH), 5.0 (1H, m, =CH), 3.65 (2H, s, CH$_2$), and 3.1 ppm (1H, s, SH). IR spectrum: 2590 (w, SH) and 1650 cm^{-1} (m, C=C).

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