REACTION FOR NUCLEOPHILIC OPENING OF THIIRANE RING BY THIOLS

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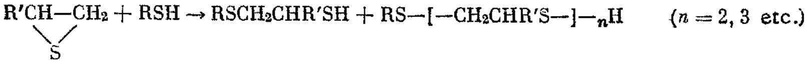
The reaction of thiiranes with H_2S and aliphatic thiols without a catalyst [1-3], and also when catalyzed by alcoholates and alkalis [2, 4-10], leads to the formation of a mixture of compounds.



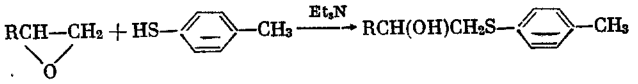
Oligomers are formed to lesser degree when reaction is with acid thiols, like dialkyldithiophosphoric acids [11] and thiophenols [12-14], in which connection the substituted thiophenols are mercaptoethylated less readily [12].

We studied the reaction of ethylene sulfide with thioacetic acid, thiophenol, and o- and p-thiocresols, and ethyl mercaptan in either benzene or THF at 45-50°C under the conditions of homogeneous catalysis with Et_3N. We made a comparative estimate of the reactivity of the oxirane and thiirane rings on the example of reaction with p-thiocresol; here the checking was done by the GLC method.

When the starting reactants are taken in stoichiometric amounts only thiophenol and p-thiocresol react unambiguously with ethylene sulfide to give the monoaddition products. With AcSH, o-thiocresol, and ethyl mercaptan the process is accompanied by oligomerization, which proceeds more intensely in THF than in benzene.

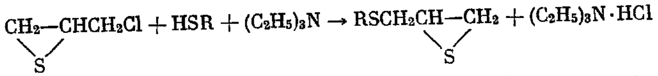
The yield of monomeric products increases in the experiments with ethyl mercaptan and o-thiocresol; when an excess of the thiol compound was used, and at certain ratios of the reactants, the monomeric products were obtained in nearly quantitative yield. This testifies to the fact that the direction of the process is determined primarily by the relation between the reactivity of the starting thiol compounds and their mercaptoethylation products. The reaction of ethylene sulfide with AcSH is accompanied by polymerization even with a 4-fold excess of the thiol compound, which can be associated with the specific traits of the mechanism for opening the ethylene sulfide ring by the thiolacetate anion.

In the reactions for the nucleophilic opening of the ring by p-thiocresol in benzene the oxiranes proved to be much more reactive compounds than the thiiranes. At 20° p-thiocresol is titrated by ethylene oxide and epichlorohydrin, which can be used in analytical practice.



$R = H, ClCH_2$

Ethylene sulfide adds p-thiocresol with noticeable speed only at 40-50°, and when the concentration of the starting compounds is reduced by half the addition is completed only after 2-2.5 h. Epithiochlorohydrin does not add p-thiocresol under these conditions, which is due to inactivation of the catalyst by the reaction:



As was established, the epithioalkanes, in contrast to the oxiranes, do not react with $Et_3N \cdot HCl$ at 40-50°.

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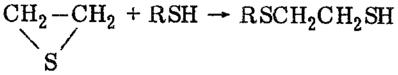
TABLE 1. Effect of Reaction Conditions on Yield of Products:



$CH_2-CH_2(S) + RSH \rightarrow RSCH_2CH_2SH$

Expt. No.	R	Ratio of reactants, reaction time, h, solvent	Yield, %	Bp, °C (p, mm of Hg)	n_D^{20}	Lit. ref.
1	C_6H_5	1 : 1, 10, benzene	90,5	91—92(1,0)	1,6154	[1]
2	"	1 : 1, 10, THF	72,4	91—92(1,0)	1,6154	[1]
3	4-$CH_3C_6H_4$—	1 : 1, 10, benzene	89,2	111(1,0)	1,6018	[12]
4	2-$CH_3C_6H_4$—	1 : 1, 10, benzene	67,9	107(1,0)	1,6079	[1]
5	"	2 : 1, 10, benzene	88,5	107(1,0)	1,6079	[1]
6	C_2H_5 —*	1 : 1, 16 benzene	54,5	71—73(15)	1,5285	[1]
7	"	1 : 1, 16, THF	42,7	—	—	[1]
8	"	4 : 1, 16, benzene	83,0	—	—	[1]

*The experiments were run in sealed glass tubes.

EXPERIMENTAL METHOD

We used freshly distilled thiol compounds that had been dried over $LiAlH_4$, THF, cryoscopic grade of anhydrous benzene, and chromatographically pure ethylene sulfide.

2,2'-Bis(acetylthio)diethyl Disulfide. A solution of 15.2 g of AcSH, 6.0 g of ethylene sulfide, and 0.5 g of Et_3N in 30 ml of benzene was heated in a dry nitrogen atmosphere at 45-50° for 10 h. The reaction mass was cooled, the polymer precipitate was separated by filtration, the solvent and excess AcSH were removed in vacuo, and the residue, after bubbling dry air through it for 6 h, was fractionally distilled. We obtained 6.2 g (46%) of 2,2'-bis(acetylthio)diethyl disulfide, bp 107° (4 mm); d_4^{20} 1.0338; n_D^{20} 1.3795. Found: S 47.06%. $C_8H_{14}O_2S_4$. Calculated: S 47.35%.

Reaction of Ethylene Sulfide with Thiol Compounds. The reaction was run the same as before, except that on the conclusion of heating the mixture was fractionally distilled in a dry nitrogen stream. The ratio of the reactants, time of heating, solvent, yield, and some of the properties of the obtained compounds are given in Table 1.

The course of the reaction of ethylene sulfide with p-thiocresol (Experiment 3) at 40-50° was followed by GLC on the basis of the amount of p-thiocresol and end product. Here we used a Tswett 4-69 chromatograph, a 3 m × 3 mm column packed with 5% SE-52 deposited on TND-TSM, helium as the carrier gas, and a flow rate of 18 ml/min. Under these conditions the amount of p-thiocresol drops by half in 20-25 min, and by 90% in 2.5 h.

2-p-Thiocresylethanol. Into a solution of 12.4 g of p-thiocresol and 0.5 g of Et_3N in 30 ml of benzene was bubbled 5 g of ethylene oxide. Distillation gave 15.5 g (97%) of 2-p-thiocresylethanol [15], bp 132-133° (4 mm); d_4^{20} 1.1084; n_D^{20} 1.5803.

2-Chloro-2-p-thiocresylisopropanol [16]. Obtained in a similar manner from 12.4 g of p-thiocresol, 10.2 g of epichlorohydrin, and 0.5 g of Et_3N in 98% yield, bp 132-133° (1 mm); d_4^{20} 1.2028; n_D^{20} 1.5796.

CONCLUSIONS

The nucleophilic opening of the thiirane ring by thiols proceeds with greater difficulty than that of the oxirane ring. Aliphatic and aromatic thiols in nonpolar solvents, using homogeneous catalysis by bases, can be unambiguously mercaptoethylated by selecting the necessary ratios of thiol compound and ethylene sulfide.

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