NUCLEOPHILIC OPENING OF THIIRANE RING BY HYDROXY COMPOUNDS

A. V. Fokin, A. F. Kolomiets, and L. S. Rudnitskaya UDC 542.91:547.379

As is known [1, 2], the 2-mercaptoalkylation of hydroxy compounds with thiiranes does not lead to the formation of monomeric compounds. The reactions of alkylene sulfides with alcohols and phenols in the presence of alkaline agents, and also with alcoholates and phenolates in aprotic solvents are accompanied by a quantitative conversion of the thiiranes to high-molecular compounds. The early communications on the formation of monomeric products [3] in these reactions proved to be wrong [4].

The polymeric transformations of thiiranes when reacted with alcoholates are explained [1] by the incomparably weaker nucleophilic properties of the alkoxide anions when compared with those of the thiolate anions formed during reaction.

In order to ascertain the character of the processes that proceed under the conditions of opening the thirane rings by alkoxide anions we studied the reactions in the systems: $CH_3ONa-ethylene$ sulfide-electrophilic reagent. The combination of the processes that proceed here can be depicted by the following system of equations.



The reactions were run in benzene in order to lower the rate of the S_N1 transformations along direction C. It was shown in advance that in benzene the opening of the ethylene sulfide ring by sodium methylate proceeds with satisfactory speed at 40-50°C, in view of which all of the reactions were run at this temperature. 1, 2-Dichloro-2-butene, benzyl chloride, and n-octyl bromide were used as the electrophilic reagents. The reactions were studied at molar ratios of CH_3ONa : ethylene sulfide: electrophilic reagent =1: 1:3.

The obtained results are given in Table 1. As was to be expected, ethylene sulfide polymers are not formed in the presence of organic halides. The ethylene sulfide conversion in the system is determined by the rate of the competing reaction C, and increases with decrease in the reactivity of the halide. Here there is a simultaneous increase both in the yield of oligomeric transformation products and in their molecular weight. Chain termination is observed even in the step of the monomeric fragments in the presence of halides of the allyl type. The S-alkylation of n-octyl bromide proceeds only in the steps of forming the oligomeric thiolate anions.

The transformations in the system: sodium phenolate—ethylene sulfide—benzyl chloride proceed more unambiguously than in the previous case. 1-Phenoxy-2-benzylthioethane is practically the sole product of this reaction (78% yield). Together with this, a small amount of oligomeric transformation products is formed.

Cyanoethylation of the hydroxy compound proved to be the sole process in the systems: methanol-(phenol)-ethylene sulfide-acrylonitrile when catalyzed by sodium (5 mole %). The ethylene sulfide was recovered almost completely in these cases.

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TABLE 1

Value of R in CH ₃ O(CH ₂ CH ₂ S) _{II} R	Ethylene sulfide con- version,%	Monomeric products, n = 1				Oligomeric products	
		yield, %	bp,°C(p, mm of Hg)	d_{4}^{20}	n_{D}^{20}	n	yield, g
$\begin{array}{c} CH_3CCl = \dot{C}HCH_2 * - \\ C_6H_5CH_2 \dagger & - \\ n - C_8H_{17} - \end{array}$	58 73 96	53‡ 44‡	$\begin{array}{c c} 76-78(2) \\ 99-102(3) \\ - \end{array}$	1,0854 1,0652 —	1,5002 1,5472	2,3 2,8 6,7	1,7 3,1 8,1

*Found: Cl 19.47; S 17.64%. Calculated: Cl 19.66; S 17.77%.

†Found S 17,42%, C10H14OS, Calculated: S 17,53%,

‡ Based on reacted ethylene sulfide,

The performed study of the reactions of ethylene sulfide with sodium methylate and phenolate in the selected systems of competing reactions confirms the previously expressed theories on the reasons for the polymerization transformations of alkylene sulfides in the reactions of their nucleophilic cleavage by hydroxy compounds. The obtained results testify to the fact that in weakly polar media the electrophilic properties of the ethylene sulfide ring toward alkoxide and aroxide anions are comparable with the electrophilic properties of the highly reactive halides of the allyl type, but substantially smaller than for acrylonitrile.

EXPERIMENTAL METHOD

Chromatographically pure ethylene sulfide and freshly distilled alkyl halides and cryoscopy grade benzene were used. The amount of ethylene sulfide in the reaction mass was determined as described in [5].

<u>1-Methoxy-2-alkylthioethane</u>. With stirring, to a solution of 6.0 g of ethylene sulfide and 0.3 mole of the organic halide in 40 ml of benzene was added at 40-45°, in an absolute nitrogen atmosphere, in drops, a solution of 2.3 g of Na in 30 ml of methanol in 35-40 min. The mixture was stirred at 45-50° for 1 h, a sample was taken to determine the ethylene sulfide, and the remainder was treated with water. The reaction products were extracted with chloroform, and the extract was dried over Na_2SO_4 , filtered, and fractionally distilled in vacuo. The products obtained in the reactions and some of their characteristics are given in Table 1.

<u>1-Phenoxy-2-benzylthioethane</u>. With stirring, to a suspension of 11.6 g of sodium phenolate in 30 ml of benzene was added in a nitrogen atmosphere a solution of 6 g of ethylene sulfide and 25.3 g of benzyl chloride in 20 ml of benzene at 50-55°. The mixture was stirred at 60° for 4 h, cooled, washed with water, then with 2% NaOH solution, and dried over Na₂SO₄. Fractional distillation in vacuo gave 19.0 g (78%) of product, bp 110-112° (10 mm); d_4^{20} 1.0871; nD^{20} 1.5782. Found: S 13.04%. $C_{15}H_{16}OS$. Calculated: S 13.12%.

CONCLUSIONS

The reactions in the systems: sodium methylate(phenolate)—ethylene sulfide—electrophilic reagent were studied. In weakly polar media the reactivity of the ethylene sulfide ring in the reactions of cleavage by alkoxide(aroxide) anions is comparable with the reactivity of such strong electrophiles as halides of the allyl type.

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