CYCLIZATION OF CROTYL PHENYL SULFIDE IN THE PRESENCE OF ACID CATALYSTS

T. Abdin, T. A. Danilova, and E. A. Viktorova

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Crotyl phenyl sulfide is converted to 2-ethyl-2,3-dihydrobenzothiophene and 2- and 4-methylthiochromans in the presence of γ -Al₂O₃ and 5, 10, and 20% ZnCl₂/Al₂O₃ at 300°C and is also isomerized to 1-butenyl- and 3-butenyl phenyl sulfides and cleaved to thiophenol.

Crotyl phenyl sulfide (I) undergoes a thio-Claisen rearrangement in the presence of nitrogen bases to give 2-ethyl-2,3-dihydrobenzothiophene (II) and 2-methylthiochroman [1, 2]. There is no information regarding the behavior of sulfide I on acid catalysts in the literature. We have shown that in the presence of γ -aluminum oxide and zinc chloride, deposited on aluminum oxide, I is converted to II and 2- and 4-methylthiochromans at 300°. In addition, it is isomerized to 1-butenyl and 3-butenyl phenyl sulfides (III, IV) and cleaved to thiophenol (Table 1).

We suppose that the formation of cyclic sulfides is the result of thio-Claisen rearrangement of I rather than the result of its direct cyclization. If the opposite were true, one should also have observed the formation of 3-ethyl-2,3-dihydrobenzothiophene, which is not present in the products of transformation of I. The formation of two intermediate thiophenols – 2-crotyl- and 2-(2-buten-3-yl)thiophenols (V, VI) – is possible in the rearrangement of sulfide I. The latter is the result either of classical Claisen rearrange—

TABLE 1. Transformations of Crotyl Phenyl Sulfide on Acid Catalysts (300°C)

Catalyst	+	Catalyzate composition, %						
	Space velocity, h ⁻¹	thio- phenol	crotyl phenyl sulfide	1-butenyl phenyl sulfide	2-ethyl-2,3 dihydroben- zothiophene	2-methyl- thiochrom- an	4-methyl- thio- chroman	2-ethyl- benzothio- phene
Al ₂ O ₃	0,1 0,2 0,3 0,5 0,7 1,2	17 14 20 5 7 7	33 27 14 52 43 48	17 15 16 22 17 22	21 31 33 13 23 15	4 6 7 3 5	2 3 4 1 2 0	2 1 2 1 1
ZnCl ₂ /Al ₂ O ₃	0,1 0,3 0,5 1,2	40 39 34 23	24 4 12 21	13 4 6 9	9 26 24 30	5 9 9 8	8 6 5	5 9 9 4
10% ZnCl ₂ /Al ₂ O ₃	0,1 0,3 0,5	64 58 71	2 6 1	2 3 1	12 11 9	12 13 11	-	6 8 6
20% ZnCl ₂ /Al ₂ O ₃	0,1 0,3 0,5* 1,2*	46 54 60 72	4 5 3 1	4 4 2 1	17 8 11 9	20 17 14 10		7 6 9 5

^{*3-}Butenyl phenyl sulfide (1% at a space velocity of 0.5 h^{-1} , and 2% at 1.2 h^{-1}) was also detected in the catalyzate.

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ment at the γ -carbon atom with inversion of the alkyl chain or at the β -carbon atom, while thiophenol V could arise only by rearrangement at the α -carbon atom with retention of the straight chain. This sort of rearrangement was described in [3]. Cyclization of V leads to II and 2-methylthiochroman; the isomeric 4-methylthiochroman is the product of cyclization of VI.

The transformations of sulfide I depend substantially on the acidity of the catalyst. Thus, in the presence of the least acidic catalyst, Al_2O_3 , the isomerization of I to III proceeds to the maximum extent (Table 1). As the acidity of the catalyst increases, the competitive process – cleavage of I to thiophenol (the ratio of cyclization products decreases) – is reinforced, 4-methylthiochroman vanishes, and the yield of 2-methylthiochroman increases. This serves as indirect proof of the absence of direct cyclization of I to 4-methylthiochroman since, if the opposite were true, the amount of the latter should have increased with increasing acidity; on the other hand, the predominance of 2-methylthiochroman indicates that thio-Claisen rearrangement on catalysts with high aprotic acidity proceeds primarily at the α -carbon atom. The ratio of II to 2-methylthiochroman also varies as a function of the catalyst acidity: II is primarily formed in the presence of Al_2O_3 ; in the case of 20% $ZnCl_2/Al_2O_3$, both sulfides are obtained in practically equal amounts. It is possible that there is partial isomerization of 2-methylthiochroman to II. The existence of a transformation of a similar nature was proved in [4]. Sulfide I is also isomerized to IV in the presence of only 10 and 20% $ZnCl_2/Al_2O_3$ at space velocities of 0.5-1.2 h^{-1} . Under these conditions, III and IV are formed in equal amounts [they were separated chromatographically with a column filled with polyethylene glycol adipate (PEGA)].

An increase in the space velocity leads to a decrease in cleavage of I to thiophenol (Table 1).

In all cases, one observes dehydrogenation of II to 2-ethylbenzothiophene and formation of gaseous hydrocarbons, which attest to cracking of the aliphatic chain. The qualitative composition of the gaseous products is constant (CH_4 , C_3H_6 , 1-butene, and 2-butene). A change in the acidity of the catalyst or in the space velocity of the process affects only the ratio of these components.

EXPERIMENTAL

The catalytic transformations of crotyl phenyl sulfide (I) were carried out with a flow apparatus with automatic feeding of the substance in a stream of nitrogen (10 ml/min). The catalyzate composition was determined by GLC at 220 and 175° with KhL-4 and KhL-6 chromatographs, respectively: with 1.8 by 4 mm steel columns and Chromosorb W (60-80 mesh) as the support and Apiezon N (15%) as the liquid support, and with 7 m by 4 mm steel columns, Chromosorb W (60-80 mesh) as the support, and PEGA (10%) as the liquid phase. The carrier gas (helium) flow rate was 43 ml/min. The individual components of the catalyzate were identified by means of standard substances. The gaseous products were analyzed with a chromatograph constructed according to the method in [5].

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