

CYCLIZATION OF CROTYL PHENYL SULFIDE IN THE PRESENCE OF ACID CATALYSTS

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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 - Al_2O_3 and 5, 10, and 20% $\text{ZnCl}_2/\text{Al}_2\text{O}_3$ 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	Space velocity, h^{-1}	Catalyzate composition, %						
		thiophenol	crotyl phenyl sulfide	1-butenyl phenyl sulfide	2-ethyl-2,3-dihydrobenzothiophene	2-methylthiochroman	4-methylthiochroman	2-ethylbenzothiophene
Al_2O_3	0.1	17	33	17	21	4	2	2
	0.2	14	27	15	31	6	3	1
	0.3	20	14	16	33	7	4	2
	0.5	5	52	22	13	3	1	1
	0.7	7	43	17	23	5	2	1
	1.2	7	48	22	15	4	0	1
5% $\text{ZnCl}_2/\text{Al}_2\text{O}_3$	0.1	40	24	13	9	5	4	5
	0.3	39	4	4	26	9	8	9
	0.5	34	12	6	24	9	6	9
	1.2	23	21	9	30	8	5	4
10% $\text{ZnCl}_2/\text{Al}_2\text{O}_3$	0.1	64	2	2	12	12	—	6
	0.3	58	6	3	11	13	—	8
	0.5	71	1	1	9	11	—	6
20% $\text{ZnCl}_2/\text{Al}_2\text{O}_3$	0.1	46	4	4	17	20	—	7
	0.3	54	5	4	8	17	—	6
	0.5*	60	3	2	11	14	—	9
	1.2*	72	1	1	9	10	—	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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