BEHAVIOR OF SULFOLANE DERIVATIVES IN THE FRIEDEL – CRAFTS REACTION

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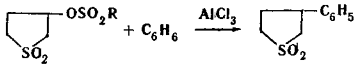
Benzene and its homologs undergo the Friedel–Crafts reaction with 3-sulfolanyl sulfonates in the presence of aluminum chloride. The chief reaction product of the reaction of 3-tosyloxysulfolane with phenol is 3-chlorosulfolane.

It has been reported [1] that methyl styryl sulfone reacts with benzene in the presence of 97% H_2SO_4 to give 76% β, β'-diphenylethyl methyl sulfone but does not react when aluminum chloride is used as the catalyst. Under similar conditions, the reaction does not proceed with methyl vinyl sulfone. There is no information available on the behavior of unsaturated cyclic sulfones or their derivatives in the Friedel–Crafts reaction.

In a study of the chemistry of sulfolane derivatives, we have found that 2-sulfolene, 3-sulfolene, and 3-methyl-3-sulfolene also do not react with benzene in the presence of 97% sulfuric acid (reagent ratio 1 : 10 : 5) even on heating to 80°C for 60 h. Pronounced resinification occurs with aluminum chloride. Traces of 3-phenylsulfolane were detected in the reaction products by means of thin-layer chromatography. Attempts to activate the reaction by prior saturation of a benzene solution of the sulfolenes with HCl, as in the reaction with acrylonitrile [2], did not give positive results. 3-Phenylsulfolane could not be obtained in experiments with 3-chloro- and 3-bromosulfolane. It was isolated in 2% quantities in the reaction with 3-hydroxysulfolane when excess (10 : 1) 97% sulfuric acid was used as the catalyst. Pronounced resinification of the reaction mass, in which traces of 3-phenylsulfolane were detected by chromatography, was observed with aluminum chloride.

Considering the increased acidity of 3-hydroxysulfolane and the associated difficulty in alkylation, we attempted to carry out the reaction with sulfolanyl esters of sulfonic [3] and carboxylic acids.

It was assumed that the introduction of sulfo and carbonyl groups, which draw off to themselves the electron pair of the carbon–oxygen bond, would promote an increase in the positive charge on the carbon atom of the sulfolanyl ring and thereby facilitate the reaction. However, arylation occurs only with sulfonates.



The sulfolanyl sulfonates (see Table 1) were obtained by the reaction of 3-hydroxysulfolane with sulfonyl chlorides in the presence of pyridine.

A temperature of 60°, an ester : aluminum chloride : benzene ratio of 1 : 2 : 7, and a reaction time of 2 h were found to be the optimum conditions in the case of the sulfolanyl ester of p-toluenesulfonic acid in the reaction with benzene. Under these conditions, there was practically no resinification when the aluminum chloride was added slowly and the reaction mass was stirred vigorously. Reactions with benzene homologs were carried out similarly. The properties of the arylsulfolanes obtained are presented in Table 2.

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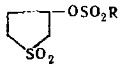
TABLE 2.



R	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	S		C	H	S	
CH_3	114,5—115,5	28,4	4,8	29,9	$C_5H_{10}O_5S_2$	28,0	4,7	29,9	70
C_6H_5	115,5—116,5	43,8	4,4	23,4	$C_{10}H_{12}O_5S_2$	43,5	4,4	23,2	89
p-$CH_3C_6H_4$	86,5—87,5*	—	—	—	$C_{11}H_{14}O_5S_2$	—	—	—	85
p-ClC_6H_4	134,5—135,5	38,9	3,7	21,3	$C_{10}H_{11}ClO_5S_2$	38,6	3,6	20,6	95

*The ester was reported in [4].

TABLE 2. 3-Arylsulfolanes

Aryl group	mp, °C	Found, %			Empirical formula	Calc., %			Yield, %
		C	H	S		C	H	S	
C_6H_5	96—97[a]	61,4	6,4	15,9	$C_{10}H_{12}O_2S$	61,2	6,1	16,4	70[b]
$CH_3C_6H_4$[c]	—	62,2	6,8	15,2	$C_{11}H_{14}O_2S$	62,8	6,7	15,2	45
2,3-$(CH_3)_2C_6H_3$	119—120	64,2	7,0	14,3	$C_{12}H_{16}O_2S$	64,2	7,2	14,3	70
2,4-$(CH_3)_2C_6H_3$	78,5—79,5	64,3	7,2	14,3	$C_{12}H_{16}O_2S$	64,2	7,2	14,3	55
2,5-$(CH_3)_2C_6H_3$	80—90	63,7	6,9	13,7	$C_{12}H_{16}O_2S$	64,2	7,2	14,3	60
2,4,6-$(CH_3)_3C_6H_2$	116—117	65,7	7,6	13,2	$C_{13}H_{18}O_2S$	65,5	7,6	13,4	50
4-i-$C_3H_7C_6H_4$	97,5—98	65,6	7,8	13,5	$C_{13}H_{18}O_2S$	65,5	7,6	13,4	50

[a] 3-Penylsulfolane was reported in [5]. [b] The yield from the reaction of benzene with the sulfolanyl ester of benzenesulfonic acid is indicated. The esters of methanesulfonic acid, p-toluenesulfonic acid, and p-chlorobenzenesulfonic acid gave 55%, 65%, and 80% yields of the 3-phenylsulfolane, respectively. [c] A mixture of o- and p-tolylsulfolanes with bp 88-100° (0.015 mm).

Except for toluene, crystalline products with sharp melting points were obtained in all cases. The experiment with toluene yielded a liquid reaction product, the IR spectrum of which contains strong bands at 740 and 760 cm^{-1}, which are characteristic for 1,2-disubstituted benzenes, and a band at 817 cm^{-1}, which is characteristic for 1,4-disubstituted aromatic compounds [6]; these data make it possible to assume the presence of a mixture of isomers. The IR spectrum of the dimethylphenylsulfolane from the experiment with o-xylene contains strong bands at 740 and 780 cm^{-1}, which are characteristic for 1,2,3-trisubstituted aromatic systems. The IR spectra of the products of the reaction with p- and m-xylenes display great similarity and contain bands at 808-820 cm^{-1} and 880-890 cm^{-1}, which are characteristic for 1,2,4-tetrasubstituted benzenes.

The reaction with phenol proceeded with pronounced resinification. 3-Chlorosulfolane was the major product isolated, along with only ~5% 3-(hydroxyphenyl)sulfolane, while the formation of only traces of 3-chlorosulfolane was observed with benzene and its homologs.

In contrast to the sulfolanyl sulfonates, the sulfolanyl benzoate is practically inert in the reaction. The sulfolanyl acetate acylates benzene partially, but the formation of 3-phenylsulfolane could not be established.

Thus, of all the sulfolane derivatives examined, the esters of sulfonic acids can be recommended as alkylating agents in the synthesis of arylsulfolanes.

EXPERIMENTAL

Sulfolanyl Esters of Sulfonic Acids (Table 1). These were obtained by the reaction of 3-hydroxysulfolane [7] with the acid chlorides of methane-, benzene-, p-toluene-, and p-chlorobenzenesulfonic acids in absolute pyridine with a reagent ratio of 1 : 1.5. The reaction times at 0-15° and room temperature were 2 h and 20 h, respectively.

Arylsulfolanes (Table 2). These were obtained by the addition of aluminum chloride in a molar ratio of 2 : 1 or 3 : 1 (with respect to the sulfonate) to a solution of the sulfonate in the aromatic compound with vigorous stirring. After hydrogen chloride evolution had ceased, the mixture was heated at 60° for 2-5 h. The end of the reaction was judged from the disappearance of a spot on the chromatogram in a thin layer of activity II-III aluminum oxide [ethyl acetate–diethyl ether system (1 : 1) with development by iodine]. The reaction mass was treated with 10% hydrochloric acid at 0°. The aqueous layer was extracted with the aromatic compound. The organic layer and the extracts were combined, dried with calcium chloride, and evaporated in vacuo. The residue was recrystallized from methanol. The product of the reaction with toluene was isolated by vacuum distillation.

The reaction with phenol yielded 3-chlorosulfolane with mp 61-61.5° [4] and hydroxyphenylsulfolane (5%) with mp 128-129°.

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