SULFOLENYL AND SULFOLANYL SULFONATES IN THE FRIEDEL–CRAFTS REACTION

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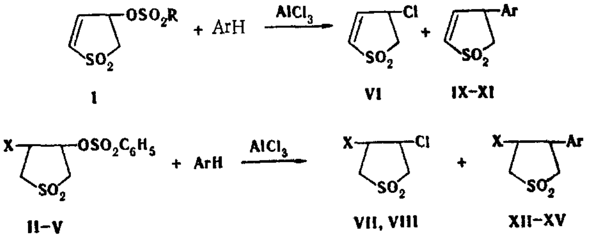
The behavior of various sulfolenyl and sulfolanyl sulfonates in the Friedel–Crafts reaction was studied. The sulfolane ring undergoes both arylation and halogenation. The ratio of reaction products depends on the nature of the starting sulfonate.

3-Sulfolanyl arenesulfonates form 3-arylsulfolanes in good yields on heating with aromatic hydrocarbons in the presence of $AlCl_3$ [1]. Arylsulfolanes could not be isolated with other sulfolane derivatives [2]. The synthesis of arylsulfolanes from arylbutadienes and sulfur dioxide has not found broad application because of the limited accessibility of arylbutadienes [3]. Considering the accessibility of sulfolenyl and substituted sulfolanyl sulfonates [4], in the present study we have investigated their behavior in the Friedel–Crafts reactions in order to obtain arylsulfolenes and substituted arylsulfolanes.



II $X=CH_3$; III $X=OH$; IV $X=Cl$; V $X=OSO_2C_6H_5$

When the reaction was carried out under the conditions in [1], we found in the case of 4-hydroxy-2-sulfolenyl sulfonates that substituents (CH_3, Cl, and NO_2) in the meta and para positions of the benzene ring of the arenesulfonate group do not have a substantial effect on the reaction with benzene and its derivatives. We therefore subsequently used benzenesulfonates. 4-Aryl-2-sulfolenes (IX–XI, see Table 1) were isolated in 75–95% yields in the reaction of I with benzene, anisole, and mesitylene. Since the possible isomerization of sulfolene derivatives in acidic media was previously reported in [5], we proved the position of the double bond in IX–XI by comparison of the physical constants and chromatographic and spectral characteristics of IX and the known 3-phenyl-3-sulfolene [3] and 3-phenyl-2-sulfolene [6]. The isomerization of IX in 1 N aqueous KOH, which, according to the data of thin-layer chromatography (TLC), gives a mixture of isomers, from which 3-phenyl-3-sulfolene and 3-phenyl-2-sulfolene are isolated with a column filled with aluminum oxide, may serve as an additional proof of the position of the double bond. In addition to 4-aryl-2-sulfolenes, a small amount of 4-chloro-2-sulfolene (VI), which was identified by means of TLC, is formed in the reaction of I with benzene.

A mixture (1.7 : 1) of 3-methyl-4-phenylsulfolane (XII) and the known 3-methyl-2-sulfolene [7], the formation of which can be explained by elimination of the sulfonate group and subsequent isomerization [8], was obtained in the reaction of II with benzene (II : $AlCl_3$ = 1 : 0.5–2).

The principal reaction products in the reaction of III–V with aromatic hydrocarbons in the presence of excess (2 : 1) $AlCl_3$ are 3-hydroxy-4-chlorosulfolane (VII) [9] with III and 3,4-dichlorosulfolane (VIII) [9]

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TABLE 1. Aryl Derivatives of the Sulfolane Series

Compound	Ar	X	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
					C	H	S	C	H	S	
IX	C_6H_5	H	84—85	$C_{10}H_{10}O_2S$	61,3	5,2	16,3	61,8	5,2	16,5	95
X	$C_6H_4OCH_3$-*p*	H	118—119	$C_{11}H_{12}O_3S$	58,5	5,4	14,6	58,6	5,7	14,2	88
XI	2,4,6-$(CH_3)_3C_6H_2$	H	174—175	$C_{13}H_{16}O_2S$	66,0	6,5	13,9	66,0	6,4	13,6	75
XII	C_6H_5	CH_3	134—135	$C_{11}H_{14}O_2S$	62,5	6,6	15,5	62,8	6,7	15,2	35
XIII	C_6H_5	OH	139—140	$C_{10}H_{12}O_3S$	56,8	5,5	15,2	56,6	5,6	15,1	33

with IV and V; this attests to predominance of chlorination over alkylation. In the case of V, pronounced resinification and H_2S evolution is observed with a greater amount (3 : 1) of $AlCl_3$.

Phenylsulfolanes XIII (X = OH) and XIV (X = Cl) are obtained in yields of 30 and 12%, respectively, when III, IV : $AlCl_3$ = 1 : 1 only on prolonged refluxing (8-36 h). With V, the starting sulfonate is regenerated under these conditions. Activation by hydrogen chloride does not lead to an increase in the yield of the phenylsulfolanes. Diphenylsulfolane XV is formed only on refluxing (60 h) with V : $AlCl_3$ = 1 : 2. Since XIV and XV could not be isolated from a mixture with VIII by crystallization, the reaction products were nitrated, and XIV and XV were identified as nitrophenylsulfolanes XVII and XVIII.

EXPERIMENTAL

Starting sulfonates I-V were previously obtained in [4]. Thin-layer and column chromatography with activity-II aluminum oxide (with diethyl ether as the eluent) were used to identify and separate the products. The thin-layer chromatograms were developed with iodine vapors.

4-Phenyl-2-sulfolene (IX). A 5.6-g (45 mmole) sample of anhydrous aluminum chloride was added gradually to a solution of 8.2 g (0.03 mole) of 2-sulfolen-4-yl benzenesulfonate in 60 ml of absolute benzene, and the mixture was refluxed for 5 h until hydrogen chloride evolution ceased. The end of the reaction was judged from the disappearance of the sulfonate spot on the thin-layer chromatogram. The reaction mixture was poured over ice and acidified with hydrochloric acid. The benzene layer was separated, and the aqueous layer was extracted with benzene (twice with 30-ml portions). The benzene solution and the extracts were combined, washed with water until neutral, and dried with anhydrous sodium sulfate. The benzene was removed in vacuo with a water aspirator, and the residue was crystallized from methanol to give 4-phenyl-2-sulfolene.

4-(p-Methoxyphenyl)-2-sulfolene (X) and 4-Mesityl-2-sulfolene (XI). These compounds were obtained by the method used to prepare IX.

3-Methyl-4-phenylsulfolane (XII). This compound was obtained by the method used to prepare IX. The residue after removal of the solvent contained a mixture of 3-methyl-2-sulfolene (R_f 0.17) and 3-methyl-4-phenylsulfolane (R_f 0.33) in a ratio of 1.7 : 1; these compounds were separated with a column.

3-Hydroxy-4-phenylsulfolane (XIII). This compound was obtained under the conditions used for the preparation of IX. The benzene solution was worked up similarly. The aqueous layer was cooled to 5°, and the resulting precipitate and the residue obtained after removal of the benzene from the organic layer by distillation were combined and chromatographed with a column (VII : XIII = 1.6 : 1).

4-(p-Nitrophenyl)-2-sulfolene (XVI). A mixture of 3 ml of nitric acid (sp. gr. 1.50) and 4.3 ml of sulfuric acid (sp. gr. 1.84) was added dropwise to an ice-cooled solution of 13.6 g (0.07 mole) of 4-phenyl-2-sulfolene in 3 ml of concentrated sulfuric acid (sp. gr. 1.84), after which the mixture was heated at 40-50° for 30 min and then poured over ice. The precipitate was removed by filtration, washed with water, and dried. Crystallization from methanol gave XVI with mp 139-140°. Found: C 50.4; H 3.9; N 6.2; S 13.5%. $C_{10}H_9O_4NS$. Calculated: C 50.2; H 3.8; N 5.9; S 13.4%.

3-Chloro-4-(p-nitrophenyl)sulfolane (XVII). A 21-g sample of a mixture of 3,4-chlorosulfolane and 3-chloro-4-phenylsulfolane, obtained by refluxing (for 36 h) 64.8 g (0.2 mole) of 3-chloro-4-hydroxysulfolanyl benzenesulfonate, 150 ml of absolute benzene, and 27 g (0.20 mole) of anhydrous aluminum chloride, was crystallized from methanol. The resulting precipitate (11.8 g) of 3,4-dichlorosulfolane was separated. The methanol was removed from the filtrate by distillation, and the residue (9.2 g) was nitrated under the conditions of the synthesis of XVI. Crystallization from methanol gave 7 g of XVII with mp 190-191°. Found: C 43.7; H 3.7; Cl 12.7; N 5.1; S 11.5%. $C_{16}H_{10}ClNO_4S$. Calculated: C 43.6; H 3.7; Cl 12.8; N 5.1; S 11.6%.

3,4-Di(p-nitrophenyl)sulfolane (XVIII). A 19-g sample of a mixture of 3,4-dichlorosulfolane and 3,4-diphenylsulfolane, obtained by refluxing (for 60 h) 64.8 g (0.15 mole) of trans-3,4-dihydroxysulfolanyl dibenzenesulfonate, 180 ml of absolute benzene, and 80 g (0.6 mole) of anhydrous aluminum chloride, was crystallized from methanol. The precipitate (7 g) of 3,4-dichlorosulfolane was separated. The methanol was removed from the filtrate by distillation, and the residue (11 g) was nitrated under the conditions of the synthesis of XVI. Crystallization from methanol gave 4.4 g of XVIII with mp 200-201°. Found: N 7.5%. $C_{16}H_{14}N_2O_6S$. Calculated: N 7.7%.

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