REACTION OF ARYLAMINES WITH SOME β,β'-SUBSTITUTED SULFOLANES AND β-SUBSTITUTED 2- AND 3-SULFOLENES

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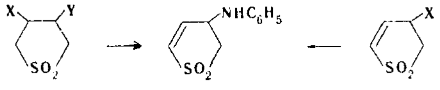
UDC 547.732:542.958.3

The reaction of β,β'-substituted sulfolanes and β-substituted 2- and 3-sulfolenes with aromatic amines was investigated. 4-Arylamino-2-sulfolenes and 3-arylamino-4-hydroxysulfolanes were obtained.

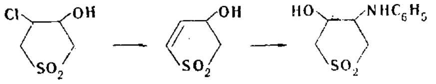
We have previously demonstrated [1] that arylaminosulfolanes are formed in the reaction of some β-substituted derivatives of sulfolane with arylamines. In order to obtain difunctional arylaminosulfolanes and arylaminosulfolenes, in the present communication we investigated the reaction of arylamines with β,β'-substituted sulfolanes (Ia-g) and β-substituted 2-sulfolenes (IIa-g) and 3-sulfolenes (XVII).



I III II

I, II a $X=Y=Br$; b $X=Y=OSO_2CH_3$; c $X=Y=OSO_2C_6H_5$; d $X=Br$, $Y=OSO_2C_6H_5$; e $X=Cl$, $Y=OSO_2C_6H_5$; f $X=Y=OCOCH_3$; g $X=Y=OCOC_6H_5$

The reaction of aniline with trans isomers Ia-c,e and cis isomers Ib,c gave 4-anilino-2-sulfolene (III), the same product that was obtained in the reactions of aniline with 2-sulfolene derivatives (IIa,c). Under similar conditions, 4-hydroxy-2-sulfolene (V) was isolated in the reaction with 3-chloro-4-hydroxysulfolane (IV), while 3-anilino-4-hydroxysulfolane (VI) was isolated from the reaction at 170-180°C.



IV V VI

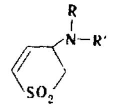
Sulfolanyl (If,g) and sulfolenyl (IIf,g) esters of carboxylic acids do not undergo reaction at 60° but undergo acyl cleavage at 170-180°, giving the amides of the acids and hydroxyl derivatives of sulfolane and sulfolene.

The reaction of Ia,b with ammonia is described in [2], while the reaction of Ia with aliphatic amines and pyridine [3], which leads to the formation of an unstable thiophene dioxide which then reacts with the amines, is described in [3]. In our experiments with aniline, we did not observe the formation of a thiophene dioxide.

Considering the reduced basicity of aniline and the associated difficulty in the addition of it to 2-sulfolene [1], it can be assumed that, except for V, in which substitution of the hydroxyl group is absent at 60°, substitution occurs with 4-substituted derivatives of 2-sulfolene (IIa,b). Nucleophilic addition of aniline at the activated double bond of V is observed at 170-180°. Elimination of one substituent and subsequent allyl substitution of the second substituent occurs with difunctional derivatives of sulfolane (Ia-e).

Institute of the Chemistry of High-Molecular-Weight Compounds, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1193-1195, September, 1972. Original article submitted July 12, 1971.

TABLE 1



Comp.	R	R′	mp, °C (from CH_3OH)	Empirical formula	Found, %		Calc., %		Yield, %
					N	S	N	S	
III	H	C_6H_5	131—132	$C_{10}H_{11}NO_2S$	6,2	15,5	6,7	15,2	92
VII	C_2H_5	C_6H_5	112—114	$C_{12}H_{15}NO_2S$	6,1	13,8	5,9	13,5	71
VIII	H	*p*-$CH_3C_6H_4$	115—116	$C_{11}H_{13}NO_2S$	6,5	14,3	6,3	14,4	94
IX	H	*m*-$CH_3C_6H_4$	169—170	$C_{11}H_{13}NO_2S$	5,9	14,5	6,3	14,4	94
X	H	*o*-$CH_3C_6H_4$	113—115	$C_{11}H_{13}NO_3S$	6,2	14,2	6,3	14,4	75
XI	H	*p*-$CH_3OC_6H_4$	128—129	$C_{11}H_{13}NO_3S$	5,8	13,3	5,8	13,3	92
XII	H	*m*-$CH_3OC_6H_4$	116—118	$C_{11}H_{13}NO_3S$	6,1	13,1	5,8	13,3	92
XIII	H	*o*-$CH_3OC_6H_4$	103—105	$C_{11}H_{13}NO_3S$	6,0	13,6	5,8	13,3	92
XIV	H	*p*-ClC_6H_4	123—125	$C_{10}H_{10}ClNO_2S$*	—	13,4	—	13,2	80
XV	H	*m*-BrC_6H_4	211—213	$C_{10}H_{10}BrNO_2S$	4,7	11,4	4,8	11,1	81
XVI	H	*o*-ClC_6H_4	103—104	$C_{10}H_{10}ClNO_2S$ †	—	13,4	—	13,2	71

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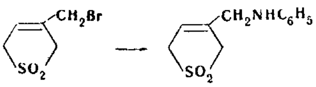
*Found: Cl 14.5%. Calculated: Cl 14.5%.

† Found: Cl 14.4%. Calculated: Cl 14.5%.

The decrease in the yield of 4-anilino-2-sulfolene (III) in the reaction with I and IIe as compared with Ia-d and IIa-c can be explained by the unequivalent tendencies of these compounds to undergo substitution. It was found that Id,e react with pyridine in dioxane when they are present in equimolar amounts to give IIc and IIe, respectively, which indicates the following order of elimination of substituents: Br > OSO_2R > Cl. If it is assumed that the rates of elimination of OSO_2R are approximately the same in the reaction of Id and Ie with aniline, the rate-determining step of the reaction should be substitution, and this is in agreement with the yields of III obtained. The reaction of 3,4-dibromosulfolane Ia with other arylamines proceeds similarly. Substituted arylaminosulfolenes VII-XVI (Table 1) are obtained. It is apparent from Table 1 that the inductive and steric effects of the substituents in the arylamines in the reaction under investigation have a smaller effect on the yield of product than in the addition to 2-sulfolene [1].

Aniline hydrobromide is formed quantitatively in the reaction of 3-methyl-3,4-dibromosulfolane with aniline, sulfur dioxide is evolved, and the products, which could not be identified, undergo resinification.

Aniline reacts vigorously with 3-bromomethyl-3-sulfolene (XVII) to give 3-phenylaminomethyl-3-sulfolene (XVIII), which is in agreement with the activity of halogen in allyl compounds [4].



In contrast to the allyl systems examined above, 3-chloro-3-sulfolene and 3-chloro-2-sulfolene did not react with aniline. The inertness of vinyl halogen and its appreciable activation of a double bond with electron-acceptor groups at the ends are well known [5]. The absence of a reaction with 3-chloro-2-sulfolene can apparently be explained by the insufficient nucleophilicity of aniline and the steric hindrance of the β-carbon atom of the sulfolane ring.

EXPERIMENTAL

4-Anilino-2-sulfolene (III). A mixture of 2.8 g (0.01 mole) of 3,4-dibromosulfolane, 2.8 g (0.05 mole) of aniline, and 2 ml of methanol was heated at 60° for 8 h. The methanol was evaporated, and the residue was washed with water to remove the aniline hydrobromide (Table 1).

Under similar conditions, III was obtained in 90-95% and 40% yields, respectively, from Ib-d, IIa and from I, IIe.

Compounds VIII-XVI were similarly obtained by the reaction of 3,4-dibromosulfolane with substituted anilines (Table 1).

3-Phenylaminomethyl-3-sulfolene (XVIII). A mixture of 1.1 g (0.005 mole) of 3-(bromomethyl)-3-sulfolene and 1.4 g (0.015 mole) of aniline was heated at 60° for 3 h in 10 ml of ethanol. The ethanol was removed by distillation, and the residue (aniline hydrobromide) was extracted with chloroform to constant weight (of aniline hydrobromide). The chloroform extract was evaporated, and the residue was crystallized to give 1 g (95%) of a product with mp 96-97° (from methanol). Found: S 14.5%. $C_{11}H_{13}NO_2S$. Calculated: S 14.3%.

3-Anilino-4-hydroxysulfolane (VI). A mixture of 1.7 g (0.01 mole) of 3-chloro-4-hydroxysulfolane and 1.9 g (0.020 mole) of aniline was heated at 170-180° for 6 h. The reaction mixture was washed with water to remove the aniline hydrochloride, and the residue was crystallized to give 1.3 g (55%) of a product with mp 127-129° (from water). Found: N 5.9; S 14.4%. $C_{10}H_{13}NO_3S$. Calculated: N 6.1; S 14.1%.

Cleavage of 4-Acetoxy-2-sulfolene (IIf). A mixture of 5.3 g (0.03 mole) of 4-acetoxy-2-sulfolene and 5.6 g (0.06 mole) of aniline was heated at 175° for 6 h. The excess aniline was removed by distillation, and the mixture was treated with ether. The insoluble residue was distilled to give 2.0 g (51%) of 4-hydroxy-2-sulfolene. The ether extract was evaporated, and the residue was crystallized. The yield of acetanilide was 3.7 g (91%).

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