SYNTHESIS OF SULFOLANE- AND SULFOLENESULFONATES

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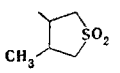
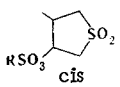
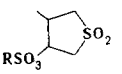
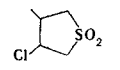
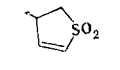
UDC 547.732.07

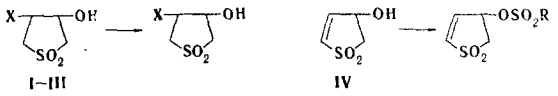
It is shown that sulfolane- and sulfolenesulfonates are stable in pyridine solutions at low temperatures. On the basis of this, a reliable method for their synthesis in 70-90% yields was developed.

It has been reported [1,2] that sulfolanyl esters of arene(alkane)sulfonic acids can be used to introduce a sulfolane ring into various classes of compounds. A new method for the preparation of arylsulfolanes, which are of interest as intermediates [3], from 3-sulfolanesulfonates has been developed. However, there is still no satisfactory method for the preparation of sulfolanesulfonates. During the synthesis of esters of p-toluenesulfonic acid and hydroxy derivatives of sulfolane (II) and sulfolene (IV) in pyridine at 0-20°C, it was found [4] that esterification is complicated by secondary reactions to give the unstable thiophene S,S-dioxide [5] and products of its subsequent transformation. This lowers the yield of sulfolanesulfonates to 30-40%. We have found that esters of hydroxysulfolanes (I-III) and hydroxysulfolene (IV) are stable in pyridine solution at about −20°; this made it possible to develop a reliable method for the preparation of various sulfolanesulfonates in high yields (70-90%).

TABLE 1. $Z = OSO_2R$

R	Z	mp, °C	Empirical formula	S, % found	S, % calc.	Yield, %
CH_3		98	$C_6H_{12}O_5S_2$	28,5	28,1	80
C_6H_5		92	$C_{11}H_{14}O_5S_2$	22,0	22,1	80
$C_6H_4CH_3$-*p*		82	$C_{12}H_{16}O_5S_2$	21,2	21,1	80
CH_3	 cis	220	$C_6H_{12}O_8S_3$	30,8	31,2	85
C_6H_5		157	$C_{16}H_{16}O_8S_3$	22,4	22,2	80
C_6H_4Cl-*p*		216	$C_{16}H_{14}Cl_2O_8S_3$	19,4	19,2	80
$C_6H_4CH_3$-*p*		167[4]				65
$C_6H_4NO_2$-*m*		245	$C_{16}H_{14}N_2O_{12}S_3$	18,5	18,4	65
CH_3	 trans	184	$C_6H_{12}O_8S_3$	30,9	31,2	75
C_6H_5		172	$C_{16}H_{16}O_8S_3$	22,3	22,2	75
$C_6H_4CH_3$-*p*		145[4]				60
C_6H_4Cl-*p*		162	$C_{16}H_{14}Cl_2O_8S_3$	19,4	19,2	75
$C_6H_4NO_2$-*m*		177	$C_{16}H_{14}N_2O_{12}S_3$	N 5.3	N 5,4	55
CH_3		164	$C_5H_9ClO_5S_2$	25,7	25,8	70
C_6H_5		133	$C_{16}H_{11}ClO_5S_2$	20,7	20,6	70
$C_6H_4CH_3$-*p*		115	$C_{11}H_{13}ClO_5S_2$	20,2	19,7	60
C_6H_4Cl-*p*		143	$C_{10}H_{10}Cl_2O_5S_2$	Cl 20,4	Cl 20,5	75
CH_3		126	$C_5H_8O_5S_2$	30,2	30,2	90
C_6H_5		116	$C_{10}H_{10}O_5S_2$	23,3	23,4	65
$C_6H_4CH_3$-*p*		138[4]				85
C_6H_4Cl-*p*		126	$C_{10}H_9ClO_5S_2$	20,5	20,8	90
$C_6H_4NO_2$-*m*		192	$C_{10}H_9NO_7S_2$	20,2	20,1	70

Institute of the Chemistry of High-Molecular-Weight Compounds, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1489-1490, November, 1972. Original article submitted October 5, 1971.



I–III IV

I a X=H; b X=CH_3; II a X=cis-OH; b X=trans-OH; III X=Cl; R=Alk, Ar

EXPERIMENTAL

The reaction was carried out at −20 to −15° by the addition of a stoichiometric amount of sulfonyl chloride to a solution of the appropriate hydroxysulfolane in pyridine. The mixture was held at −15 to −5° for 2 h and was then poured over ice. The sulfolanesulfonate was removed by filtration, washed successively with dilute (1 : 5) sulfuric acid and water, and crystallized from alcohol. The compounds obtained are presented in Table 1.

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