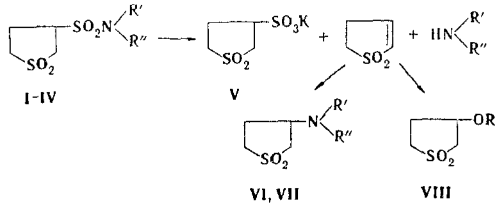
HYDROLYSIS OF SULFOLANESULFONAMIDES

T. É. Bezmenova, L. P. Matyash,
and A. Ya. Bezmenov

UDC 547.732:542.938

Under alkaline hydrolysis conditions, alkyl- and dialkylamides of sulfolanesulfonic acid form a sulfolanesulfonic acid salt and alkyl- or dialkylaminosulfolanes, respectively.

The exchange reactions of sulfolanyl esters, amines, and sulfones with several nucleophilic reagents were described in [1, 2]. In the present paper the possibility of the exchange of the sulfamide group of amides of sulfolane-3-sulfonic acids (I-IV) by amino and alkoxyl groups under conditions of alkaline hydrolysis, aminolysis, and alcoholysis is demonstrated.



I, VI $R'=H$; $R''=C_4H_9$; II, VII $R'=R''=C_2H_5$; III $R'=R''=H$; IV $R'=H$; $R''=C_6H_5$; VIII $R=n\text{-}C_4H_9$

The sulfolanesulfonamides (I-IV) were obtained by the reaction of sulfolanesulfonyl chloride with the appropriate amine [3].

When the butylamide (I) and diethylamide (II) are heated in 1 N potassium hydroxide solution, potassium sulfolanesulfonate (V) and, respectively, butyl aminosulfolane (VI) and diethylaminosulfolane (VII), which were identified as hydrochlorides from the IR spectra and mixed-melting-point determination with compounds synthesized by alternative synthesis from 3-sulfolene [4], were isolated. Only salt V was obtained with amides III-IV.

Considering the tendency of several β-heteroatomic derivatives of sulfolane to undergo elimination [2], it can be assumed that 2-sulfolene and the amine formed during the hydrolysis of the amides participate in the formation of butylaminosulfolane (VI) and diethylaminosulfolane (VII).

In order to elucidate the mechanism of the reaction, the reaction of n-butylamine and diethylamine with the sulfolanesulfonic acid salt (V) and amides (I, II) under conditions close to hydrolysis conditions was investigated. It was found that amines do not react with V, while V forms the corresponding alkylaminosulfolanes (VI, VII) with amides. The yield of VI and VII increases appreciably in excess butylamine or diethylamine with an equimolar amount of KOH or potassium metal. Under these conditions, salt V is practically completely regenerated. Thus, 2-sulfolene was detected by thin-layer chromatography (TLC) in the aminolysis and hydrolysis products, and the formation of alkylaminosulfolane (VI, VII) can be explained by splitting out of a sulfamide group and subsequent addition of amines to the resulting 2-sulfolene.

The β-elimination of a sulfamide group in sulfone $p\text{-}CH_3C_6H_4SO_2CH_2CH_2SO_2NR_2$ has been noted [5]. It is known [3, 4] that 2-sulfolene reacts readily with primary and secondary aliphatic amines in aqueous solution, slowly with ammonium hydroxide, and does not react with aniline up to 100° [6]. This is in agreement with the proposed reaction scheme.

Institute of the Chemistry of High-Molecular-Weight Compounds, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1351-1352, October, 1972. Original article submitted July 12, 1971.

Thus, in contrast to amides of alkane(arene)sulfonic acids, the amides of sulfolane-3-sulfonic acid display increased lability of the C–N bond attached to the sulfolane ring in basic media. This conclusion is also confirmed by the reaction of I-III with potassium butoxide, which leads to the formation of butoxysulfolane (VIII). Amides I-IV are stable in acidic media, for example, in refluxing 3 N hydrochloric acid.

EXPERIMENTAL

Sulfolane-3-sulfonamides (I-IV). These compounds were obtained via the method in [3] by reaction of sulfolanesulfonyl chloride with the appropriate amines. Compound I was obtained in 75% yield and had mp 76-77° (from water). Found: C 37.6; H 7.6; S 24.8%. $C_8H_{17}NO_4S_2$. Calculated: C 37.6; H 6.7; S 25.1%. Compound II was obtained in 85% yield and had mp 78-79°. Found: C 37.5; H 7.4; S 24.8%. Compound III had mp 137-138° (mp 137-139° [3]). Compound IV had mp 118-119°.

Potassium Sulfolane-3-sulfonate (V). A mixture of 12 g (0.1 mole) of 3-sulfolene and 65 ml of 20% K_2SO_3 solution was heated at 50-60° for 3-4 h. The mixture was extracted with chloroform to remove the unchanged sulfolene, and the water was slowly evaporated to precipitate 70-80% of V. Compound V was crystallized from water. Found: C 20.1; H 3.4; S 26.6%. $C_4H_7KO_5S_2$. Calculated: C 20.2; H 3.0; S 27.3%. The IR spectra contain the characteristic frequencies of the SO_2 group at 1130 and 1300 cm^{-1} and of the SO_3 group at 1195 cm^{-1}.

Hydrolysis of I-V. A 0.02-mole sample of the product was heated in 30 ml of 1 N KOH at 70° for 6 h. The mixture was cooled and extracted with chloroform–ether (1 : 1). The water was evaporated, and the residue was crystallized from water. The sulfolanesulfonate salt was identified from the IR spectrum. The extract after removal of the solvents contained a mixture of amine (VI or VII) with 2-sulfolene; the latter was identified by TLC on activity II Al_2O_3 with elution by ether (R_f 0.38). The amine was separated from the 2-sulfolene as the hydrochloride by treatment with an acetone solution of HCl. The hydrochloride of VI had mp 136-137°, while the hydrochloride of VII had mp 148-149° [4]. Compound I yielded 20% VI and 75% V, II yielded 22% VIII and 70% V, and III-IV yielded 80-85% V. Compound V was practically completely regenerated.

Aminolysis of I-III and V. A 0.02-mole sample of the product was heated with saturated aqueous NaOH or R'R''NNa in a molar ratio of 1 : 0.1 or 1 : 1 in 20-50 ml of butylamine or diethylamine at 60-70° for 6 h. The mixture was then vacuum-evaporated, and the residue was worked up as described above for the hydrolysis. The yields of VI and VII from I-III were 55-65%. The starting material was quantitatively regenerated from V.

Alcoholysis of Compounds I-III and V. A 0.04-mole sample of the product was similarly heated with sodium butoxide (1 : 1) in 50 ml of butanol. The mixture was worked up by the method described above. Butoxysulfolane (VIII) with bp 148-150° (2 mm), n_D^{20} 1.4711, and d_4^{20} 1.146 was obtained in 60-65% yield from I-III. Found: S 17.1%; MR_D 46.9. $C_8H_{16}O_3S$. Calculated: S 16.7%; MR_D 46.9. The starting material was regenerated in the case of V.

LITERATURE CITED

1. T. É. Bezmenova, R. A. Dorofeeva, and A. Ya. Bezmenov, Zh. Organ. Khim., 3, 778 (1967).
2. T. É. Bezmenova, P. G. Dul'nev, L. P. Matyash, M. V. Rybakova, and T. N. Varshavets, Summaries of Papers Presented at the 12th Scientific Session on the Chemistry and Technology of Organic Sulfur Compounds [in Russian], Riga (1971), p. 165.
3. C. A. Argule, S. C. Goadby, K. G. Mason, R. A. Reed, M. A. Smith, and E. S. Stern, J. Chem. Soc., 21C, 2156 (1967).
4. M. L. Leffler and W. D. Krueger, J. Am. Chem. Soc., 71, 370 (1949).
5. D. C. Campbell and C. J. Stirling, J. Chem. Soc., 5869 (1964).
6. T. É. Bezmenova and P. G. Dul'nev, Dokl. Akad. Nauk Ukr. SSR, 34, 45 (1972).