

FORMATION OF AMMONIUM SALTS OF 2-AMINO-3-FORMYLBUTANESULFINIC  
ACIDS IN THE REACTION OF 3-METHYL-2,3-EPOXYSULFOLANE  
WITH AMINES

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The reaction of 3-methyl-2,3-epoxysulfolane with amines proceeds with opening of not only the epoxide ring but also opening of the sulfolane ring to give the corresponding salts of 2-amino-3-formylbutanesulfinic acids.

We have previously shown that the reaction of 3,4-epoxysulfolanes with amines proceeds through the intermediate formation of the corresponding unsaturated alcohols with the subsequent addition of the amine to the double bond [1]. In order to ascertain the effect of the sulfonyl group on opening of the adjacent oxide ring under the influence of amines we studied the reaction of 3-methyl-2,3-epoxysulfolane (I) with propylamine, diethylamine, piperidine, and morpholine.

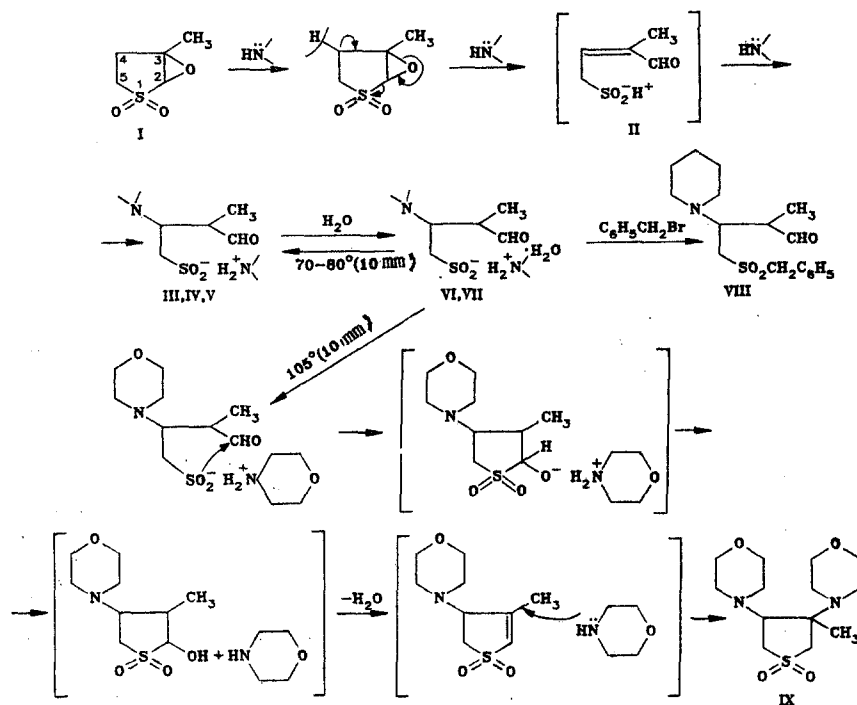
In contrast to 3,4-epoxysulfolanes, which react with amines to give the corresponding hydroxyaminosulfolanes [1], the reaction of epoxide I with amines proceeds with opening of not only the epoxide ring but also opening of the sulfolane ring to give ammonium 2-amino-3-formylbutanesulfinates III, VI, and VII. Crystalline VI and VII are formed in the action of heterocyclic amines, viz., piperidine and morpholine, on the investigated epoxide, whereas glassy substance III is formed in the case of the action of propylamine. The reaction does not proceed with diethylamine at atmospheric pressure, and pronounced resinification of the reaction mixture and the partial formation of a salt structure are observed under more severe conditions (at increased pressure and at temperatures above 100°C).

The structures of salts III, VI, and VII are in agreement with the spectral data and were confirmed chemically. Very intense broad bands at 960 and 1010  $\text{cm}^{-1}$ , which are characteristic for the  $\text{SO}_2^-$  grouping, in contrast to the absorption at 1130 and 1300  $\text{cm}^{-1}$  that is usually observed for the sulfonyl group in sulfones [2], are observed in their IR spectra. A broad multiplet band at 2000-3200  $\text{cm}^{-1}$ , which is characteristic for ammonium salt structures [2], and absorption due to a carbonyl group at 1720-1730  $\text{cm}^{-1}$  also appear in the spectra. The shift of the band of carbonyl absorption to the low-frequency region (1680  $\text{cm}^{-1}$ ) in the case of III can be explained by strengthening of the hydrogen bonds. In addition, a band of vibrations of hydroxy groups at 3300-3500  $\text{cm}^{-1}$ , which is due to the presence of crystallization water in the molecule and vanishes in the spectra of dehydrated salts IV and V, is observed in the IR spectra of salts VI and VII. Glassy substances IV and V, which were obtained as a result of heating crystal hydrates VI and VII *in vacuo* at 60-90°C, crystallize rapidly in air to give salts VI and VII once again. A signal at 9.3-9.8 ppm, which corresponds to the resonance of the proton of an aldehyde group [3], is present in the PMR spectra of III, VI, and VII. The presence of this group is also confirmed by a positive reaction with Tollens reagent [4].

The action of benzyl bromide on salt VI led to the formation of 2-piperidino-3-formylbutyl benzyl sulfone (VIII). The absorption band of a carbonyl group at 1730  $\text{cm}^{-1}$  is retained in its IR spectrum, but bands at 1100 and 1290  $\text{cm}^{-1}$ , which are characteristic for a sulfonyl group, appear instead of a band of a  $\text{SO}_2^-$  grouping. Heating salt VII *in vacuo* at 105°C led to the development of a sulfolane ring to give 3-methyl-3,4-dimorpholinosulfolane (IX). Bands of carbonyl and hydroxy absorption vanish in its IR spectrum, while bands at 1100-1200 and 1280-1300  $\text{cm}^{-1}$ , which are peculiar to the vibrations of a sulfonyl group, appear.

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Thus, on the basis of the examined data, the following scheme for the reaction of 3-methyl-2,3-epoxysulfolane with amines can be presented:



Detachment of a proton from the C<sub>(4)</sub> atom in epoxide I under the influence of a base and subsequent redistribution of the electrons with internal nucleophilic substitution of the sulfur atom lead to cleavage of the C<sub>(3)</sub>-O and C<sub>(2)</sub>-S bonds to give intermediate II, which, as a result of addition of the reagent to two reaction centers (the double bond and the acidic function), is then converted to the corresponding sulfinate.

The formation of such salts has been noted for cyclic unsaturated sulfones when they are treated with strong bases [5].

Compound IX is evidently formed under heating conditions due to attack by sulfinate sulfur on the carbon atom of the aldehyde group with the development of a C-S bond [6] and subsequent dehydration, which leads to an unsaturated sulfone, to the double bond of which morpholine subsequently adds [1].

#### EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds between KBr plates were recorded with a UR-20 spectrometer. The PMR spectra of solutions of the compounds in CCl<sub>4</sub>, pyridine, or d<sub>6</sub>-DMSO were recorded with a Varian T-60 spectrometer with tetramethylsilane as the internal standard.

3-Methyl-2,3-epoxysulfolane (I). This compound, with mp 73-75°C, was previously obtained by the method in [7].

n-Propylammonium 2-n-Propylamino-3-formylbutanesulfinate (III). A mixture of 3 g (20 mmole) of epoxide I, 4 g (68 mmole) of n-propylamine, and 1.5 ml of water was maintained at room temperature for 1 month, after which the excess reagent and water were removed in vacuo to give 4 g (70%) of glassy substance III with  $n_D^{20}$  1.4900. IR spectrum: 960, 1015 (SO<sub>2</sub><sup>-</sup>); 1680 (CO); 2000-3200 (NH<sub>2</sub>); 3300 cm<sup>-1</sup> (NH). Found: C 50.2; H 10.1; N 10.8; S 12.0%. C<sub>11</sub>H<sub>26</sub>N<sub>2</sub>O<sub>3</sub>S. Calculated: C 49.6; H 9.8; N 10.5; S 12.0%.

Piperidinium 2-Piperidino-3-formylbutanesulfinate (VI). Similarly, from a mixture of 5 g (34 mmole) of epoxide I, 30 ml of piperidine, and 1 ml of water, after maintenance at room temperature for 1.5 months, we isolated 9.37 g (82%) of salt VI with mp 65-67°C (from benzene). IR spectrum: 950-1000 (SO<sub>2</sub><sup>-</sup>), 1720 (CO), 2000-3200 (NH<sub>2</sub>), and 3300-3500 cm<sup>-1</sup> (OH). Found: C 53.8; H 9.2; N 8.6; S 9.6%. C<sub>15</sub>H<sub>30</sub>N<sub>2</sub>O<sub>3</sub>S·H<sub>2</sub>O. Calculated: C 53.5; H 9.6; N 8.3; S 9.5%.

Removal of the crystallization water from crystal hydrate VI at 60–70°C (~10 mm) in the course of 3 h gave glassy substance IV, in the IR spectrum of which (in a stream of dry argon) the band of hydroxy absorption was virtually absent; all of the remaining frequencies were unchanged.

Morpholinium 2-Morpholino-3-formylbutanesulfinate (VII). Similarly, from 5 g (34 mmole) of epoxide I in 50 ml of morpholine with 1 ml of water after maintenance at room temperature for 1 month we isolated 7.54 g (66%) of salt VII with mp 85–87°C (from acetone). IR spectrum: 960, 1020 ( $\text{SO}_2^-$ ); 1730 (CO); 2000–3200 ( $\text{NH}_2$ ); 330–3600  $\text{cm}^{-1}$  (OH). Found: 45.7; H 8.1; N 8.0; S 9.8%.  $\text{C}_{13}\text{H}_{26}\text{N}_2\text{O}_5\text{S}\cdot\text{H}_2\text{O}$ . Calculated: C 45.9; H 3.8; N 8.2; S 9.4%.

Heating salt VII at 90°C (10 mm) for 3.5 h gave dehydrated substance V.

3-Methyl-3,4-dimorpholinosulfolane (IX). Heating 1 g of salt V at 105°C (10 mm) for 1.5 h gave 0.6 g (59%) of sulfone IX with mp 153–155°C. IR spectrum: 1100–1120, 1280–1300  $\text{cm}^{-1}$  ( $\text{SO}_2$ ). Found: C 51.1; H 7.9; N 9.6; S 10.7%.  $\text{C}_{13}\text{H}_{24}\text{N}_2\text{O}_4\text{S}$ . Calculated: C 51.3; H 7.9; N 9.2; S 10.5%.

2-Piperidino-3-formylbutyl Benzyl Sulfone (VIII). A solution of 3 g (9 mmole) of salt VI and 2 g (12 mmole) of benzyl bromide in 30 ml of absolute methanol was refluxed at 80°C for 3 h, after which it was concentrated *in vacuo*. Treatment of the residue with ether yielded 1.2 g (42%) of benzyl sulfone (VIII) with mp 92–93°C (from ether). Found: C 63.4; H 7.8; N 4.6; S 10.3%.  $\text{C}_{17}\text{H}_{25}\text{NO}_2\text{S}$ . Calculated: C 63.1; H 7.8; N 4.3; S 9.9%.

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