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Abstract

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Stereospecific Elimination of Sulfinic Acids from 1,2-Disulfones

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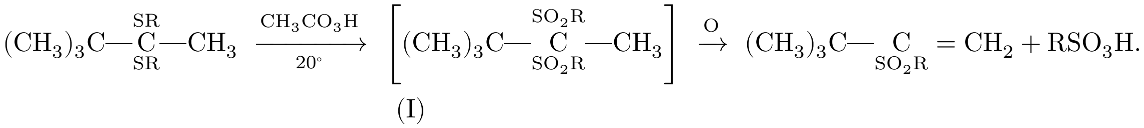
We reported earlier (¹) that disulfones of the structure $(CH_3)_3C—C(SO_2R)_2CH_3$ cannot be obtained by oxidation of the corresponding mercaptols, since under the reaction conditions they undergo various transformations, in particular oxidative cleavage:

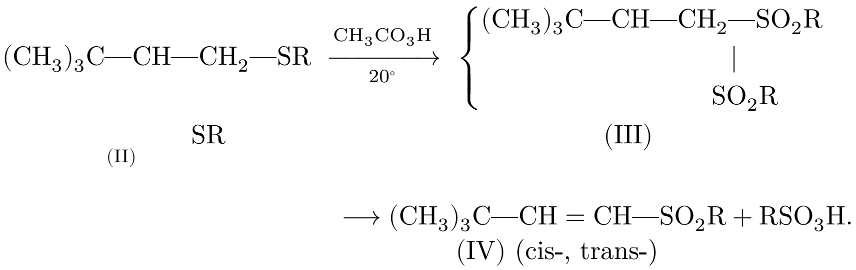


$$(CH_3)_3C—\overset{SR}{\underset{SR}{C}}—CH_3 \xrightarrow[20^\circ]{CH_3CO_3H} \left[(CH_3)_3C—\overset{SO_2R}{\underset{SO_2R}{C}}—CH_3\right] \xrightarrow{O} (CH_3)_3C—\underset{SO_2R}{C}=CH_2 + RSO_3H. \quad (1)$$

$$R = C_2H_5,\ n\text{-}C_3H_7,\ n\text{-}C_4H_9.$$

There it was also suggested that the instability of disulfones (I) is due to the steric influence of the bulky tert-butyl group, since these compounds are analogues of sulfones (²), which are more stable compounds.

In the present work the properties of 1,2-disulfones $(CH_3)_3C—CH(SO_2R)CH_2SO_2R$ (III), in which one RSO_2 group is located next to the tert-butyl group, are considered. Disulfones (III) were synthesized by oxidation of the corresponding 1,2-dithioethers (II) (³) with acetyl hydroperoxide in ether solution (reaction 2):



$$\underset{(II)}{(CH_3)_3C—\underset{SR}{CH}—CH_2—SR} \xrightarrow[20^\circ]{CH_3CO_3H} \left\{ \underset{(III)}{(CH_3)_3C—\underset{SO_2R}{CH}—CH_2—SO_2R} \right. \quad (2)$$

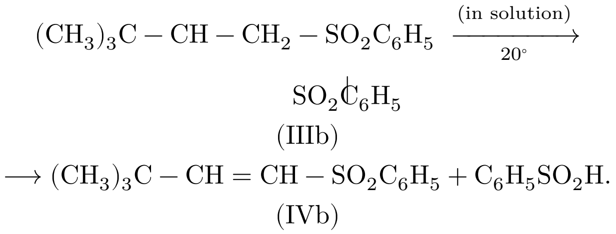
$$\longrightarrow \underset{(IV)\ (cis\text{-},\ trans\text{-})}{(CH_3)_3C—CH=CH—SO_2R + RSO_3H.}$$

$$\text{a) } R = C_2H_5,\ n\text{-}C_3H_7,\ n\text{-}C_4H_9; \quad \text{b) } R = C_6H_5.$$

It was observed that, along with the target products (III), unsaturated sulfones (IV) are formed, the yield of which depends on the structure and properties of the radical R. If R is a normal alkyl radical, then on oxidation of such dithioethers (IIa) exclusively 1,2-disulfones (IIIa) (^{3}) and only traces of unsaturated sulfones (IVa) are formed. In the case where R = C_6H_5, the oxidation reaction is accompanied by considerable cleavage, with elimination of the RS group located in the α-position to the tert-butyl group. This indicates that the steric effect of the latter creates an additional stimulus for elimination. Apparently, disulfones R'—$CH(SO_2R)CH_2SO_2R$, where R' is normal alkyl, are more stable compounds.

Disulfones (III) are crystalline or thick oily substances, insoluble in water and unchanged in air. But in organic solvents they behave differently. At the time

Since disulfones (IIIa) are stable in ether solutions, disulfone (IIIb) decomposes during storage. On chromatography on plates of a freshly prepared solution of this substance, a distinct spot with R_f value 0.15 (2 : 1)* is obtained, whereas analysis of a sample that had been stored for a month reveals one more spot, characteristic of sulfone (IVb), with R_f value 0.41 (2 : 1). Cleavage of the disulfone is accelerated if chloroform or acetone, in which the substance is more readily soluble, is used as the solvent. The reaction proceeds according to scheme (3):

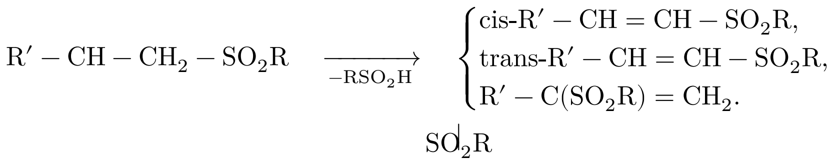


$$\underset{\text{(IIIb)}}{(CH_3)_3C-\underset{SO_2C_6H_5}{CH}-CH_2-SO_2C_6H_5} \xrightarrow[20^\circ]{\text{(in solution)}} \underset{\text{(IVb)}}{(CH_3)_3C-CH=CH-SO_2C_6H_5} + C_6H_5SO_2H. \qquad (3)$$

Fig. 1. Two-dimensional chromatogram of the products of cleavage of disulfone (III, $R = n\text{-}C_4H_9$) on a plate.
a–$(CH_3)_3C-CH(SO_2C_4H_9)CH_2SO_2C_4H_9$;
b–trans-$(CH_3)_3C-CH=CH-SO_2C_4H_9$;
c–cis-$(CH_3)_3C-CH=CH-SO_2C_4H_9$;
d–$(CH_3)_3C-C(SO_2C_4H_9)=CH_2$.

The cis- and trans-sulfones (IVb) are noncrystallizing oily substances and, on chromatography on plates, give practically coincident spots; it is therefore difficult to say in the form of which isomer sulfone (IVb) is formed in reaction (3).

The reaction of stereospecific elimination of sulfinic acids from 1,2-disulfones (III) on alumina proved to be of interest. It had been noted earlier (4) that, in an attempt to isolate from a mixture 1,2-disulfone (III, $R = n\text{-}C_4H_9$) by chromatography on an Al_2O_3 column, trans-sulfone (IV, $R = n\text{-}C_4H_9$) was obtained. It was of interest to investigate this reaction in greater detail, since theoretically one could expect cleavage of 1,2-disulfones according to scheme (4):



$$R'-\underset{\displaystyle SO_2R}{\underset{|}{CH}}-CH_2-SO_2R \xrightarrow[-RSO_2H]{} \begin{cases} \text{cis-}R'-CH=CH-SO_2R,\\ \text{trans-}R'-CH=CH-SO_2R,\\ R'-C(SO_2R)=CH_2. \end{cases} \tag{4}$$

It was also necessary to clarify the behavior of Al_2O_3 toward 1,2-disulfones and toward cis-sulfones, since the reaction might proceed, for example, with formation of cis-sulfones, while the latter might isomerize on Al_2O_3 into trans-sulfones. To resolve these questions we used the method of thin-layer chromatography of sulfones on plates with an unfixed layer of adsorbent (5). The reactions were carried out directly on the plates. Pure disulfones (III) were investigated, and the decomposition products were compared with deliberately prepared α- and cis-, trans-β-sulfones (5). Chromatography was carried out in two mutually perpendicular directions and two-dimensional chromatograms were obtained. Figure 1 presents a two-dimensional chromatogram of individual sulfones (b, c, d) and of the reaction products of disulfone (III, $R = n\text{-}C_4H_9$) on a plate. The dashed line denotes spots that would appear after chromatography of a mixture of substances (a, b, c, d) in direction 1. Substances that did not undergo changes on the plate over 6 hours, were located along the diagonal. On the chromatogram a spot is clearly distinguished which did not fall on the diagonal. It belongs to the trans-sulfone (IV, $R = n\text{-}C_4H_9$), formed as a result of decomposition of the disulfone (a), and corresponds to substance (b).

Thus it was established that 1,2-disulfones (III) do not change during chromatography on alumina plates, but on prolonged exposure to Al_2O_3 (6–12 hours) they undergo decomposition with formation exclusively of trans-sulfones (IV):

$$\underset{\text{(III)}}{(CH_3)_3C-CH(SO_2R)-CH_2-SO_2R} \xrightarrow[20^\circ]{Al_2O_3} \underset{\text{(IV)}}{\text{trans-}(CH_3)_3C-CH=CH-SO_2R}+RSO_2H. \tag{5}$$

* The R_f value was determined under the following conditions: Al_2O_3 of activity grade II; system—petroleum ether : ether = 2 : 1 (1 : 2).

Under these conditions unsaturated sulfones do not change, and cis–trans isomerization is absent.

During column chromatography the disulfones (III) are quantitatively cleaved according to equation (5), and the cis-sulfones are not isomerized into trans-sulfones. This is evidenced by the previously performed successful isolation of cis isomers from a mixture of α- and cis-, trans-β-sulfones (5). The mechanism of action of alumina apparently consists in the sulfinic acids being adsorbed more strongly on Al_2O_3, thereby causing a shift in equilibrium. As the disulfone moves down the column, the acids are retained by the adsorbent, while the trans-sulfones are isolated in quantitative yield.

The reaction (5) considered here is characterized by a high degree of stereospecificity; therefore it can serve as a preparative method for the synthesis of individual trans-β-substituted vinyl alkyl(aryl) sulfones.

Experimental Part

The following substances were investigated in this work: 1,2-bis(ethylsulfonyl)-3,3-dimethylbutane, m.p. 82–82.5° (3); 1,2-bis(n-propylsulfonyl)-3,3-dimethylbutane*

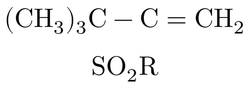
$$n_D^{20}\ 1.4886,\quad d_4^{20}\ 1.1404,\quad MR_D\ 75.50,\ \text{calculated } 75.36.$$

Found, %: C 48.53, 48.52; H 8.67, 8.90; S 21.43, 21.18
$C_{12}H_{26}O_4S_2$. Calculated, %: C 48.29; H 8.79; S 21.49

1,2-bis(n-butylsulfonyl)-3,3-dimethylbutane, n_D^{20} 1.4867, d_4^{20} 1.1092 (3); 1,2-bis(phenylsulfonyl)-3,3-dimethylbutane, m.p. 117.5–118°.

Cleavage of 1,2-disulfones on plates. Adsorbent—Al_2O_3 of the 2nd activity grade; solvent system—petroleum ether : ether = 2 : 1. Plates 20 × 20 cm in size; layer thickness 0.5 mm.

On the plate, in the lower left corner, solutions of the following substances were applied at one point: 1,2-disulfone (III), cis-, trans-sulfones (IV) (5), and α-sulfone



$$(CH_3)_3C-\underset{SO_2R}{C}=CH_2$$

(1), in a ratio of 2 : 1 : 1 : 1, and chromatographed in direction 1 (Fig. 1, R = n-C_4H_9). After the solvent had wetted the whole plate, it was kept in the chamber for 6 hours. During this time the disulfone underwent reaction in solution on alumina. The plate was removed and, after evaporation of the solvent, chromatographed in direction 2, developed, and a two-dimensional chromatogram was obtained.

Cleavage of 1,2-disulfones on a column. The column (2.5 × 60 cm) was packed with alumina (2nd activity grade) by the wet method, and a weighed sample of the substance was chromatographed according to method (5). Ratio substance : adsorbent ~ 1 : 300. Eluent—a mixture of petroleum ether and ether (1 : 1).

* Obtained by oxidation of 1,2-bis(*n*-propylthio)-3,3-dimethylbutane (3).

a) Disulfone (III, R = C_2H_5). 1.08 g of substance, 300 g of Al_2O_3. Isolated 0.70 g (99.3%) of trans-1-ethylsulfonyl-3,3-dimethylbutene-1, m.p. 55-55.5°, R_f 0.38 (1 : 2). A mixed sample showed no depression of the melting point. Literature data (5): m.p. 55.5°.

b) Disulfone (III, R = n-C_3H_7). 1.02 g of substance, 300 g of Al_2O_3. Obtained 0.64 g (98.5%) of trans-1-*n*-propylsulfonyl-3,3-dimethylbutene-1, m.p. 37-37.5°, R_f 0.48 (1 : 2). A mixed sample showed no depression of the melting point. Literature data (5): m.p. 37.5°.

c) Disulfone (III, R = n-C_4H_9). 1.22 g of substance, 350 g of Al_2O_3. Isolated 0.75 g (98.7%) of trans-1-*n*-butylsulfonyl-3,3-dimethylbutene-1, m.p. 28-29°, R_f 0.53 (1 : 2). A mixed sample with an authentic specimen showed no depression of the melting point. Literature data (5): m.p. 29°.

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