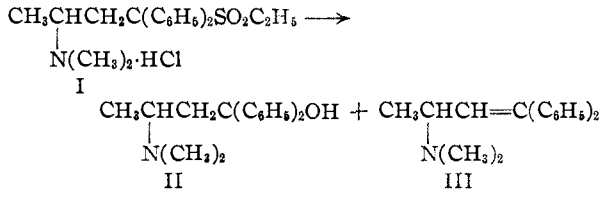
NOTES

The Cleavage of 3-Dimethylamino-1,1-diphenylbutyl Ethyl Sulfone

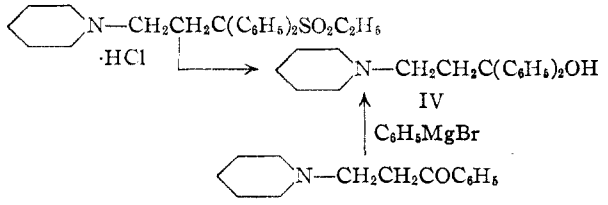
BY S. ARCHER AND M. E. AUERBACH

It is well known that drastic conditions are required to cleave most sulfones.[1] It was observed that after an aqueous solution of *l*-3-dimethylamino-1,1-diphenylbutyl ethyl sulfone hydrochloride[2] (I), had been kept at 120° for fifteen minutes the sign of rotation had changed from minus to plus. A gummy precipitate, obviously a mixture, was thrown down with ammonium hydroxide. The mixture was resolved into two components, a crystalline solid and a viscous oil, with the aid of petroleum ether. A solution of the crystalline material was moderately levorotatory, but a solution of the oil was strongly dextrorotatory.

The analytical data for the crystalline substance agreed well with the expression, II. Although the



structure of this base was not established conclusively, proof for an analogous case was obtained by direct comparison with a known sample. Ethyl-3-piperidyl-1,1-diphenylpropyl sulfone hydrochloride[3] was refluxed in aqueous solution. The carbinol base IV was isolated and proved to be identical with an authentic specimen prepared by Ruddy[4] from phenyl 2-piperidylethyl ketone and phenylmagnesium bromide.



The dextrorotatory oily base, which was the minor component of the mixture, furnished a picrate in 92% yield. The analytical results were compatible with formula III. The ultraviolet absorption spectrum resembled that obtained from 1,1-diphenylethylene.[5] Dehydration of the carbinol, II, by Adamson's method,[6] yielded the unsaturated derivative in 89% yield. These data strongly support formula III as the correct one for the oily substance.

(1) C. M. Suter, "The Organic Chemistry of Sulfur," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 683.

(2) B. F. Tullar, W. Wetterau and S. Archer, THIS JOURNAL, **70**, 3959 (1948).

(3) M. M. Klenk, C. M. Suter and S. Archer, *ibid.*, **70**, 3846 (1948).

(4) A. W. Ruddy and J. S. Buckley, Jr., *ibid.*, **72**, 718 (1950).

(5) R. N. Jones, *ibid.*, **65**, 1818 (1943).

(6) D. W. Adamson, *J. Chem. Soc.*, Suppl. 144 (1949).

Experimental[7]

Isolation of 3-Dimethylamino-1,1-diphenyl-1-butanol and 3-Dimethylamino-1,1-diphenyl-1-butene.—To 400 ml. of a 2% aqueous solution of *l*-3-dimethylamino-1,1-diphenylbutyl ethyl sulfone hydrochloride, which had been previously heated at 120° for 15 minutes in an autoclave, there was added excess ammonium hydroxide. The cloudy mixture was allowed to cool overnight. The tacky solid was removed by filtration and then dried in a desiccator; wt. 5.31 g. The dry product was triturated with 50 ml. of ligroin and then filtered. The filtrate was concentrated to dryness and heated with 30 ml. of petroleum ether. On cooling a small amount of crystalline material separated. This was collected on a filter and combined with the first crop to furnish a total of 3.73 g. of crystalline material. This was the aminocarbinol. After two recrystallizations from methanol the substance melted at 150.6–152.2° (cor.).

Anal. Calcd. for $C_{18}H_{23}NO$: C, 80.25; H, 8.61; N, 5.20. Found: C, 80.38; H, 8.69; N, 5.11; $[\alpha]^{24}D$ −32.5° (1% in ethanol); $[\alpha]^{24}D$ −41.1° (2.27% in aqueous hydrochloric acid).

The petroleum ether filtrate was taken to dryness. The residual viscous oil weighed 1.49 g.; $[\alpha]^{25}D$ +149° (1% in ethanol). Light absorption[8]: minimum, λ 232 mμ, ε 11,561; maximum λ 250 mμ, ε 12,960 (in ethanol).

The picrate was prepared from 125 mg. of the base and 5 ml. of saturated alcoholic picric acid; yield 220 mg. After recrystallization from ethanol the salt melted at 168.6–170.0° (cor.).

Anal. Calcd. for $C_{18}H_{21}N \cdot C_6H_3N_3O_7$: N_{AP}, 2.91. Found: N_{AP},[9] 2.86.

***dl*-3-Dimethylamino-1,1-diphenyl-1-butanol.**—A solution of 200 mg. of *dl*-3-dimethylamino-1,1-diphenylbutyl ethyl sulfone hydrochloride in 20 ml. of water was refluxed for one hour. The cooled solution was treated with ammonia. An oil separated which solidified on standing. After recrystallization from dilute methanol, the carbinol melted at 123.6–125.2° (cor.).

Anal. Calcd. for $C_{18}H_{23}NO$: N, 5.20. Found: N, 5.28.

Hydrolytic Decomposition of Ethyl 1,1-Diphenyl-3-piperidylpropylsulfone Hydrochloride. Isolation of 1,1-Diphenyl-3-piperidylpropanol.—A solution of 1.70 g. of the sulfone hydrochloride in 34 ml. of water was heated for three hours and then made alkaline with ammonia. The oil that separated soon solidified. It was collected on a filter and recrystallized from dilute methanol; m.p. 119–120.4° (cor.). A sample prepared by Dr. Ruddy[4] *via* the Grignard reaction did not depress the melting point of the above sample.

Anal. Calcd. for $C_{20}H_{25}NO$: N, 4.74. Found: N, 4.50.

***d*-3-Dimethylamino-1,1-diphenyl-1-butene from *l*-3-Dimethylamino-1,1-diphenyl-1-butanol.**—Three grams of the carbinol, II, was refluxed in a solution of 6.0 ml. of concentrated hydrochloric acid and 20 ml. of acetic acid for one-half hour. The solution was taken to dryness. The residue was dissolved in water, made alkaline and ether extracted. The ether solution was dried and concentrated *in vacuo*. The oily residue was dissolved in a small amount of alcohol and treated with an excess of alcoholic picric acid. The solution was heated to boiling and then allowed to cool. A total of 4.80 g. of the picrate was collected (yield 89%). After recrystallization for ethanol the salt melted at 164.5° (uncor.) and did not depress the m.p. of the sample prepared by decomposition of the sulfone (*vide supra*).

STERLING-WINTHROP RESEARCH INSTITUTE
RENSSELAER, N. Y. RECEIVED NOVEMBER 3, 1950

(7) The microanalyses were carried out under the supervision of Mr. K. D. Fleischer.

(8) We wish to thank Dr. F. C. Nachod of this Institute for these data.

(9) Perchloric acid titration for amino nitrogen.