tosylate[9] in 300 ml. of dry 5:1 ether–benzene at −30° was added dropwise 70 ml. of 1.5 *M* methyllithium (0.1 mole) in ether. A vigorous, exothermic reaction took place while the addition was carried out. At the end of the addition period the reaction mixture was allowed to warm up to room temperature and was then poured into 250 ml. of ice-water. The organic layer was separated, dried over Na_2SO_4, and evaporated at reduced pressure to a dark oil which was then stirred with 25 ml. of 1 *N* HCl for 1 hr. The acidic solution was extracted with ether to remove neutral material and was then made strongly basic and reextracted with ether. No cyclooctanone was found in the first extract. The second extract was evaporated to a dark oil which was treated with benzenesulfonyl chloride in aqueous sodium hydroxide. The basic aqueous solution was separated from insoluble material and upon acidification gave only a small amount of benzenesulfonic acid. The insoluble material yielded, after recrystallization from ethanol, 7.2 grams (71%) of a benzenesulfonamide of a secondary amine, m.p. 84°.

Anal. Calcd. for $C_{16}H_{25}NO_2S$ (295.44): C, 65.04; H, 8.41; N, 4.74; S, 10.85. Found: C, 64.70; H, 7.79; N, 5.08; S, 10.69.

Reaction of Cyclooctanone Oxime Tosylate with Phenyllithium.—A solution of 5.0 g. (0.017 mole) of cyclooctanone oxime tosylate in 150 ml. of dry ether and 50 ml. of dry benzene was cooled to −30°. With stirring under nitrogen 35 ml. of 1.5 *M* phenyllithium (0.05 mole) in ether was added dropwise over 15 min. No evolution of heat occurred when the reagent was added. The mixture was very slowly warmed to room temperature and stirred for 5 hr. The crude product was processed in the same manner as in the preceeding experiment and yielded 3.7 g. (62%) of a benzenesulfonamide, m.p. 140° (ethanol).

Anal. Calcd. for $C_{20}H_{25}NO_3S$ (359.48): C, 66.82; H, 7.01; N, 3.90. Found: C, 66.85; H, 7.04; N, 4.00.

Acknowledgment.—The author would like to thank Professor G. L. Closs for suggesting this problem.

(9) (a) P. W. Neber and G. Huh, *Ann.*, **515**, 283 (1935); (b) P. Oxley and W. F. Short, *J. Chem. Soc.*, 1514 (1948); (c) W. Z. Heldt, *J. Am. Chem. Soc.*, **80**, 5880 (1958).

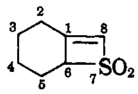
A New Bicyclic Thiete Sulfone[1]

DONALD C. DITTMER AND FRANKLIN A. DAVIS

Department of Chemistry, Syracuse University, Syracuse, New York 13210

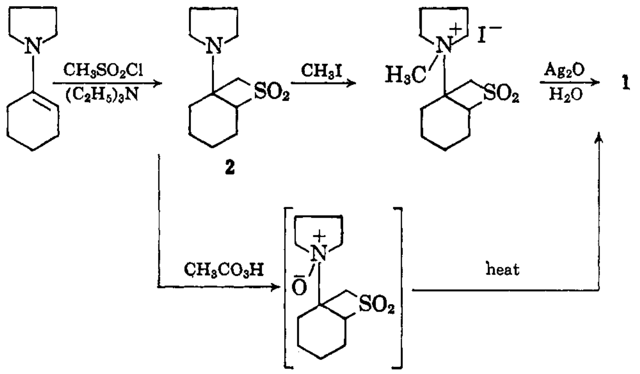
Received May 12, 1964

Only four reports of the synthesis of thiete sulfone (thiacyclobutene 1,1-dioxide) derivatives, all monocyclic, are found in the literature.[2–5] We were interested in the preparation of substituted thiete sulfones since these compounds might not undergo ring opening on reduction with lithium aluminum hydride as do several of the more simple derivatives.[4,6] Reports by Stork and Borowitz[7] and by Opitz and Adolf[8] of the synthesis of aminothietane sulfones by reaction of enamines with methanesulfonyl chloride in the presence of a base prompted us to apply this method to the synthesis of the bicyclic thiete sulfone, 7-thiabicyclo-[4.2.0]-1(8)-octene 7,7-dioxide (**1**).



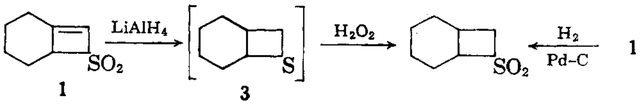
1

The reaction of methanesulfonyl chloride with cyclohexanone pyrrolidine enamine[9] in benzene in the presence of triethylamine gave an 80% yield of the cyclic sulfone **2**. Treatment of **2** with methyl iodide in methyl ethyl ketone gave the quaternary salt (30% yield) which was stirred overnight with freshly prepared silver oxide to yield, upon heating to 40–50°, the thiete sulfone **1**, in 35–40% yield. A better procedure is to convert the intermediate amine **2** to the amine oxide which on heating is converted to the unsaturated sulfone in 55–65% yield.



The structure of the bicyclic thiete sulfone **1** was supported by its infrared spectrum, proton magnetic resonance spectrum, elemental analysis, and molecular weight. Its infrared spectrum showed absorption at an olefinic C–H stretching frequency of 3003 cm.$^{-1}$ and at a C–C double bond stretching frequency of 1608 cm.$^{-1}$. The proton n.m.r. spectrum provides further proof that the double bond is *exo* to the six-membered ring. Absorption (at 60 Mc. relative to tetramethylsilane) occurs at δ 2.0 (relative area 8, protons of cyclohexane ring), 4.5 (relative area 1, 6-proton), and 6.2 (relative area 1, 8-proton). Had the double bond been between carbons 1 and 6, only two principal proton absorptions would have been observed in the ratio 8:2. The *exo* product is the one expected on the basis of a *trans* elimination of N-methylpyrrolidine.

Reduction of **1** with lithium aluminum hydride gives an oil (lacking infrared absorption for a sulfone or an olefin) which can be oxidized to a sulfone which is identical with the product obtained on catalytic reduction of the double bond of **1**. This result strongly suggests that the oil has structure **3**, and that this reduction of a thiete sulfone with lithium aluminum hydride is the first one which occurs without opening of the four-membered ring. The fused six-membered ring may hinder attack on the 6-position by hydride ion



---

(1) This work was supported by Grant GP-726 of the National Science Foundation.

(2) D. C. Dittmer and M. E. Christy, *J. Org. Chem.*, **26**, 1324 (1961).

(3) W. E. Truce, J. R. Norell, J. E. Richman, and J. P. Walsh, *Tetrahedron Letters*, 1677 (1963).

(4) W. E. Truce and J. R. Norell, *J. Am. Chem. Soc.*, **85**, 3236 (1963).

(5) R. H. Hasek, P. G. Gott, R. H. Meen, and J. C. Martin, *J. Org. Chem.*, **28**, 2496 (1963).

(6) D. C. Dittmer and M. E. Christy, *J. Am. Chem. Soc.*, **84**, 399 (1962).

(7) G. Stork and I. J. Borowitz, *ibid.*, **84**, 313 (1962).

(8) G. Opitz and H. Adolph, *Angew. Chem.*, **74**, 27 (1962).

(9) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Am. Chem. Soc.*, **85**, 207 (1963).

(complexed with aluminum) which had been suggested to account for the ring opening.[6] This reduction is under study. Further work is in progress on the chemistry of this new bicyclic unsaturated sulfone.

Experimental

Cyclohexanone pyrrolidine enamine is prepared from pyrrolidine and cyclohexanone.[9] Triethylamine is dried over potassium hydroxide, and methanesulfonyl chloride and methyl iodide are used as obtained. Silver oxide is prepared as described in *Organic Reactions*.[10] Commercial 40% peracetic is used as obtained.

Cyclohexanone Pyrrolidine Enamine Sulfone (2).—Methanesulfonyl chloride (114.0 g., 1.00 mole) in 300 ml. of dry benzene is added dropwise with stirring to triethylamine (151.5 g., 1.5 moles) and cyclohexanone pyrrolidine enamine (151.0 g., 1.0 mole) in 1000 ml. of dry benzene. The reaction mixture is cooled in an ice bath during the addition and is done in an atmosphere of dry nitrogen. After the addition of methanesulfonyl chloride the reaction mixture is stirred overnight in the ice bath. The triethylamine hydrochloride is removed by filtration and washed with benzene. These washings are combined with the filtrate and the benzene is removed on a rotary evaporator at a bath temperature below 40°. The last traces of solvent are removed under high vacuum. The light yellow sirup is dissolved in absolute ethanol and allowed to crystallize at 0° to give 172 g. (0.750 mole, 75%) of colorless crystals, m.p. 42–43°.

Anal. Calcd. for $C_{11}H_{19}NO_2S$: C, 57.59; H, 8.35; N, 6.12; S, 13.98. Found: C, 57.49; H, 8.26; N, 6.12; S, 13.85.

Quaternary Salt of 2.—A slight excess of methyl iodide is added to cyclohexanone pyrrolidine enamine sulfone (5.0 g., 0.022 mole) in 100 ml. of methyl ethyl ketone. Use of ether or 1,2-dimethoxyethane as solvent is less satisfactory. After 2 days at room temperature, the salt is removed by filtration and recrystallized from ethanol–ether to give 2.5 g. (0.0067 mole, 30%) of colorless crystals, m.p. 168–170°.

Anal. Calcd. for $C_{12}H_{22}INSO_2$: C, 38.32; H, 5.97; N, 3.78; S, 8.63. Found: C, 38.59; H, 6.07; N, 3.82; S, 8.84.

7-Thiabicyclo[4.2.0]-1(8)-octene 7,7-Dioxide (1). A.—Freshly prepared silver oxide[10] (13.3 g., 0.058 mole) is added with stirring to the quaternary iodide (10.0 g., 0.027 mole) of **2** in 200 ml. of water through which nitrogen has been passed. The reaction mixture is stirred for 12 hr. and the precipitated salts are removed by filtration, heated under vacuum (water pump) at 50° for 1 hr., cooled, and extracted with chloroform. The chloroform extracts are dried over calcium sulfate and evaporated to a clear sirup which is recrystallized from ether to yield 1.7 g. (0.011 mole, 41%) of white crystals of the bicyclic sulfone, m.p. 88–89°.

The infrared spectrum of the sulfone showed absorption at 3003 (s), 2933 (m), 2841 (w), 1608 (w–m), 1443–1422 (m), 1328 (m), 1292 (vs), 1225–1200 (vs), 1170 (vs), 1140 (s), 1070 (m), 1042 (w), and 927 (m) cm.$^{-1}$. The proton n.m.r. spectrum in $CDCl_3$ (tetramethylsilane reference) showed complex absorption from 60 to 175, complex absorption at 268, and a doublet (J_{86} = 2 c.p.s.) at 377 c.p.s. The relative areas were 8:1:1 respectively. The coupling constant, J_{86} = 2 c.p.s., is about that expected in a thiete sulfone for a 1,5-interaction.[2]

Anal. Calcd. for $C_7H_{10}O_2S$: C, 53.14; H, 6.37; S, 20.27; mol. wt. (boiling point elevation in bromoform), 158. Found: C, 53.28; H, 6.48; S, 20.16; mol. wt., 165.

B.—Peracetic acid (20 ml., 40%) is added dropwise during 30 min. to cyclohexanone pyrrolidine enamine sulfone **2** (10 g., 0.044 mole) in a 125-ml. erlenmeyer flask cooled in an ice–salt bath. After addition of the peracetic acid, the mixture is kept in the bath for an additional 30 min. and at room temperature for 4 hr. Glacial acetic acid (10 ml.) is added, and the mixture is cooled and neutralized with saturated sodium carbonate solution. The solution is heated at 60° under vacuum (water pump) for 2 hr., cooled, saturated with sodium chloride, and extracted with chloroform or ether. The extracts are washed with 10% hydrochloric acid and dried over sodium carbonate. Removal of the solvent leaves 4.0 g. (0.025 mole, 57%) of white needles, m.p. 85–88°. The infrared spectrum was identical with the product obtained by the Hofmann elimination procedure.

Reduction of the Bicyclic Thiete Sulfone (1) **with Lithium Aluminum Hydride.**—The thiete sulfone 1 (3.0 g., 0.019 mole) in 100 ml. of dry ether is added to lithium aluminum hydride (2.3 g., 0.058 mole) in 50 ml. of dry ether. The hydride and ether have been refluxed for 30 min. prior to the addition. The reaction mixture is stirred for 3 hr. at room temperature followed by destruction of the excess hydride by successive additions of 20 ml. of ammonium chloride (20% solution) and 2 ml. of concentrated ammonium hydroxide in 5 ml. of the ammonium chloride solution. Evaporation of the ether layer, after it is dried over calcium chloride, gives a yellow oil (**3**, 2.1 g.). The infrared spectrum of the oil shows bands at 2940 (s), 1450 (m), 1310 (w), 1270 (w), 1160 (w), and 1140 (w) cm.$^{-1}$.

Oxidation of the Lithium Aluminum Hydride Reduction Product.—Hydrogen peroxide (30%, 1.62 g., 0.0143 mole) is added to 10 ml. of a solution of acetic acid and 0.6 g. of the oil obtained on reduction of the bicyclic thiete sulfone with lithium aluminum hydride. The mixture is heated for 1 hr. at about 100° and allowed to stir at room temperature overnight. The reaction mixture is poured into water, made basic with 20% sodium hydroxide, and extracted with ether. The ether extract is dried and evaporated to give 0.7 g. of a pale yellow liquid which solidifies at about 10°. The infrared spectrum of the oil shows absorption at 2941 (s), 2865 (m), 1449 (m), 1414 (m), 1309 (s), 1294 (s), 1212 (m), 1193 (m), 1160 (s), 1139 (s), 1105 (m), and 762 (m) cm.$^{-1}$.

Reduction of 1 With Hydrogen.—Hydrogenation of 1 (3.0 g., 0.019 mole) in 50 ml. of absolute ethanol at 40 p.s.i. over 50 mg. of 10% palladium on charcoal for 4 days yields a clear oil which solidifies at 10° and crystallizes from ether at −10°. The infrared spectrum is identical with that of the product of the oxidation of the material obtained on reduction of 1 with lithium aluminum hydride.

Anal. Calcd. for $C_7H_{12}O_2S$: C, 52.48; H, 7.55. Found: C, 52.50; H, 7.58.

---

(10) A. C. Cope and E. R. Trumbull, *Org. Reactions*, **11**, 317 (1960).