

of benzene or toluene was added in portions. The temperature was kept below 25 °C by cooling in ice water. The mixture was left for 3–4 h and then heated, a gas burette being attached to the top of the reflux condenser. Nitrogen evolution started at 50–90 °C. The gas evolution was allowed to proceed at a brisk rate by gradual heating, giving a total reaction time of less than 4 h. The isocyanate was separated from the solvent by distillation through a 30 cm stainless steel spiral column having 5 mm internal diameter. Because of the instability of isocyanates, yields were variable but usually better than 50 %.

To obtain a better determination of the yields, the Curtius rearrangement was repeated (on a 7 mmol scale). After the nitrogen evolution had ceased, a slight excess of aniline was added to the reaction mixture. The resulting *N*-alkyl-*N'*-phenyl urea was freed from tetrabutylammonium chloride by washing the solution with water. The organic solvent was evaporated and the resulting product recrystallized from aqueous ethanol. The yields of the urea derivatives obtained are given in Table 1. The reaction with aniline is assumed to be quantitative,⁷ and the recrystallization losses are small. The identity was further verified by ¹H NMR.

Acknowledgement. We thank Professors Lars Melander and Martin Nilsson for their constructive criticism.

1. Smith, P. A. S. *Org. React.* 3 (1946) 337, p. 373.
2. van Reijendam, J. W. and Baardman, F. *Synthesis* (1973) 413.
3. Sakai, K. and Anselme, J. P. *J. Org. Chem.* 36 (1971) 2387.
4. Hughes, E. D., Ingold, C. K., Mak, S. F., Patai, S. and Pocker, Y. *J. Chem. Soc.* (1957) 1220.
5. Opitz, G., Griesinger, A. and Schubert, H. W. *Justus Liebig's Ann. Chem.* 665 (1963) 91.
6. Gutmann, V., Hampel, G. and Leitmann, O. *Monatsh. Chem.* 95 (1964) 1034.
7. Petersen, S. In Houben-Weyl: *Methoden der Organischen Chemie*, 4th Ed., Part 8, III, Georg Thieme, Stuttgart 1952, p. 157.
8. Jensen, K., Due, M. and Holm, A. *Acta Chem. Scand.* 19 (1965) 438.

Received June 4, 1974.

Reinvestigation of the Synthesis of Thiete 1,1-Dioxide

BO LAMM and KENNETH GUSTAFSSON

Department of Organic Chemistry, Chalmers University of Technology and University of Göteborg, Fack, S-402 20 Göteborg 5, Sweden

The four-membered cyclic unsaturated title compound was needed as a synthetic intermediate in our work. Dittmer and Christy^{1,2} first prepared it as indicated in Fig. 1. Since

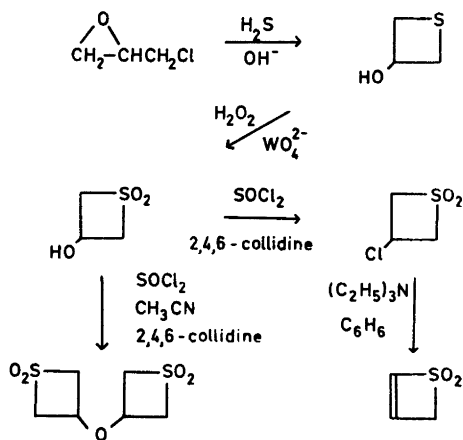


Fig. 1. Synthetic route to thiete 1,1-dioxide and bis-(3-thietanyl 1,1-dioxide) ether.

the yield in the first step was only 39 %, and since the second step involved a reportedly³ hazardous evaporation of peracetic acid, an alternative synthetic route was later described.³ This starts with a 2 + 2 cycloaddition of sulfene to *N,N*-dimethylvinylamine. The latter compound is very unstable, requiring low temperature and oxygen-free conditions, and we did not deem a large-scale preparation attractive.

Upon reinvestigation of the original procedure, we found that the first step is much more conveniently carried out in potassium hydroxide solution than with barium hydroxide.¹ The reaction of epichlorohydrin with hydrogen sulfide in basic solution was first described by Sjöberg.⁴ He obtained 30 % yield with potassium hydroxide, but a much higher yield, 65 %, is actually secured by continuous extraction of the aqueous phase with ether.

The second step, oxidation of 3-thietanol to the sulfone, can advantageously be carried out with 30 % aqueous hydrogen peroxide and a catalytic amount of sodium tungstate⁵ instead of the usual mixture of aqueous hydrogen peroxide and acetic acid.¹

Upon an attempted preparation of 3-chlorothietane 1,1-dioxide in acetonitrile as solvent, the hitherto unreported bis-(3-thietanyl 1,1-dioxide) ether was obtained instead of the chloro compound. This ether was characterized through its spectral data (IR, 60 MHz ^1H NMR, and high-resolution MS). The analogous sulfide is known.⁶

It is possible that in acetonitrile, the 3-thietanol 1,1-dioxide anion can compete with chloride ion in the decomposition of the chlorosulfite ester initially formed from 3-thietanol 1,1-dioxide and thionyl chloride, since the alcohol is soluble in acetonitrile. The desired chloro compound is formed only under "dry" conditions.

Experimental. *3-Thietanol.* A solution of 200 g of potassium hydroxide (3 mol, assuming 15 % moisture content) in 900 ml of water was saturated with hydrogen sulfide. Epichlorohydrin, 143 g (1.54 mol), was added dropwise during 2 h with good stirring and simultaneous introduction of hydrogen sulfide. The temperature gradually rose to 60 °C in this process. A slow stream of hydrogen sulfide was introduced for 1 h, and the mixture left overnight. It was then exhaustively extracted with ether, a continuously working apparatus being used. The ether was removed *in vacuo* and the remainder distilled to yield 91 g of 3-thietanol (65 % yield), b.p. 95–97 °C at 3.3 kPa (25 mmHg).

3-Thietanol 1,1-dioxide. Of the preceding compound, 90 g (1 mol) was dissolved in 500 ml of water containing 2 g of sodium tungstate and about 0.5 ml of glacial acetic acid; pH 4–5. While stirring well and maintaining the temperature at 20 °C with a glass cooling coil, 250 ml of 30 % hydrogen peroxide (appr. 2.5 mol) was added during 1 h. The reaction mixture was watched for 5 h and cooled as required to maintain the temperature at 20 °C. It was then left overnight. After decantation from a small amount of a sticky, white by-product, excess peroxide was destroyed with a pinch of palladium on carbon. After a negative peroxide test, the colourless solution was evaporated *in vacuo* at a temperature not exceeding 40 °C. *Since explosions have been reported to occur in the similar preparation using acetic acid-hydrogen peroxide,² we earnestly urge the reader to take necessary precautions.* The evaporation of 1 mol batches has been carried out four times without incidents.

The remainder after evaporation consisted of a colourless crystalline material and a small amount of a likewise colourless oil. The crystals were brought into solution with boiling ethyl acetate and decanted from the oil. Upon cooling, large crystals were obtained, m.p. 100 °C, lit.¹ 99.5–102 °C, yield 75 g (61 %).

3-Chlorothietane 1,1-dioxide. The directions in Ref. 1 were closely followed. With 20 g batches, the yield was typically 77 %, lit.¹ 86 %, m.p. 135–137 °, lit.¹ 136.5–137.5 °C.

Thiete 1,1-dioxide. Also this compound was prepared according to Ref. 1. Recrystallization from ether containing a few per cent ethanol gave a fraction m.p. 49–50 °C, lit.¹ 48–50 °C, representing 63 % yield, lit.¹ 81 %. From the mother liquor, a second crop was secured, m.p. 45–50 °C, 27 % yield.

Bis-(3-thietanyl 1,1-dioxide) ether. 3-Thietanol, 5 g (0.041 mol) and redistilled 2,4,6-collidine, 5 g (0.041 mol) were dissolved in 50 ml of dry acetonitrile. A solution of 9.8 g (0.082 mol) of thionyl chloride in 25 ml of acetonitrile was added dropwise during 30 min with stirring and cooling in ice. A crystalline precipitate was formed during the addition but disappeared when the mixture was heated in a boiling water bath for 30 min. The resulting clear solution was evaporated at aspirator vacuum, and the solid remainder triturated with cold water. A greyish, insoluble material was filtered off and recrystallized from boiling water with charcoal decolorization. White needles were obtained, yield 0.6 g (13 %), m.p. 165–165.5 °C (Kofler Hot Stage). One further recrystallization did not change the m.p. The 60 MHz ^1H NMR spectrum in deuterated dimethyl sulfoxide consisted of a complex pattern at δ 4.1–5.0 and another one at δ 5.2–5.6, the integrals of which were in the ratio 4:1. The IR spectrum (KBr disc) had two broad bands, characteristic of sulfones, at 1120–1160 and 1300–1340 cm^{-1} , and a band with peaks at 1210 and 1230 cm^{-1} which can be ascribed to an ether structure. In the region above 1450 cm^{-1} , only two bands at 2970 and 3040 cm^{-1} , typical of C–H stretching, were apparent but no hydroxyl band. The high-resolution mass spectrum was obtained with an AEI MS 902 instrument, using 50 eV electrons for ionization and a heated direct insertion probe. The fragmentation pattern was found to be very dependent on the probe temperature. A very low intensity $M+1$ peak appeared at 150 °C (not visible at lower temperatures), measured mass 227.008, rel. height 0.03 % ($\text{C}_8\text{H}_{11}\text{S}_2\text{O}_4 = 227.005$). No parent peak was visible. Fragment peaks were apparent at 168.9634 mass units, 4.12 % ($\text{C}_5\text{H}_5\text{S}_2\text{O}_4 = 168.9629$); 148.0202, 0.59 % ($\text{C}_5\text{H}_5\text{SO}_3 = 148.0194$); 123.0119, 1.03 % ($\text{C}_3\text{H}_3\text{SO}_3 = 123.0116$); 104.9983, 14.0 % ($\text{C}_2\text{H}_2\text{SO}_3 = 105.0010$); 94.0085, 8.1 % ($\text{C}_2\text{H}_2\text{SO}_2 = 94.0088$); 78.9854, 6.3 % ($\text{CH}_3\text{SO}_2 = 78.9853$); 75.9986, 10.7 % ($\text{C}_2\text{H}_4\text{SO} = 75.9989$); and 63.9623, 100 % ($\text{SO}_2 = 63.9619$). The $\text{C}_8\text{H}_{11}\text{S}_2\text{O}_4$ peak is thought to result from a rearrangement procedure.

Acknowledgements. Financial support from the Swedish Natural Science Research Council is gratefully acknowledged. The mass spectrum determination was carried out by Mr. W. Pimlott at the Department of Medical Membrane Chemistry, University of Göteborg. His help in interpreting the data is much ap-

preciated. Mr. P. Bergmark assisted in the preparative work and is also thanked.

1. Dittmer, D. C. and Christy, M. E. *J. Org. Chem.* **26** (1961) 1324.
2. Dittmer, D. C., Christy, M. E., Takashina, N., Henion, R. S. and Balquist, J. M. *J. Org. Chem.* **36** (1971) 1324.
3. Chang, P. L. F. and Dittmer, D. C. *J. Org. Chem.* **34** (1969) 2791.
4. Sjöberg, B. *Über Thioglycerine*, Diss., Lund 1941.
5. Schultz, H., Freyermuth, H. and Buc, S. *J. Org. Chem.* **28** (1963) 1140.
6. Dittmer, D. C. and Christy, M. E. *J. Amer. Chem. Soc.* **84** (1962) 399.

Received April 24, 1974.