Tetrahedron Letters No. 25, pp. 1677-1679, 1963. Pergamon Press Ltd.
Printed in Great Britain.

THIETENE 1,1-DIOXIDES VIA HOFMANN ELIMINATION

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(Received 5 August 1963)

Thietene 1,1-dioxide (I), 

, has been synthesized[3], but by a multi-step route involving the reaction of an alkali metal sulfide on epichlorohydrin to form 3-thietanol, followed by oxidation, chlorination and dehydrohalogenation. The overall yields are low and we have encountered some difficulty in duplicating the results, particularly in the oxidation step. No other detailed syntheses of thiacyclobutene derivatives has appeared and analogs of I have not been described.

We should now like to report a comparatively simple approach for the preparation of thietene 1,1-dioxides involving the reaction of sulfonyl chlorides with enamines to form 3-aminothietane 1,1-dioxides[4] followed by the Hofmann elimination[5] on the corresponding quaternary

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[1] Post-doctoral research assistant supported by grant No. CY-4536 from the National Institutes of Health.

[2] Participant in Undergraduate Research Participation Program sponsored by the National Science Foundation, 1963.

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

[4] G. Stork and I. J. Borowitz, *J. Am. Chem. Soc.*, **84**, 313 (1962); G. Opitz and H. Adolph, *Angew. Chem.*, **74**, 77 (1962).

[5] A. C. Cope and E. R. Trumbull, *Org. Reactions*, **11**, Chap. 5 (1960).

ammonium salts. For example, when an ethereal solution of methanesulfonyl chloride was added to an equimolar solution of triethylamine and N,N-dimethylisobutenyl amine[6] in ether, a white precipitate of triethylamine hydrochloride was obtained. Removal of the salt and evaporation of solvent.resulted in a pale yellow oil, which could be distilled to give the colorless 2,2-dimethyl-3-dimethylaminothietane 1,1-dioxide (II) in 75-80% conversion, b.p. 80-81° (0.3 mm.), n_D^{20} 1.4810. The n.m.r. and infrared spectra substantiated the assigned structure. *Anal.* Calcd. for $C_7H_{15}NSO_2$: C, 47.44; H, 8.53; N, 7.91; S, 18.06; M.W., 177.2. Found: C, 47.29; H, 8.79; N, 8.13; S, 17.85; M.W., 181.9 (Osmometer in $CHCl_3$).

Methiodide III was formed in 61% yield by quaternization of II with excess methyl iodide in methanol and could be readily recrystallized from methanol, m.p. 210-211° (dec.). The Hofmann elimination was easily effected by stirring III with an aqueous suspension of silver oxide followed by filtration of inorganic salt and warming the filtrate to 40° under reduced pressure (water pump) for 15 minutes so as to remove triethylamine. Extraction with methylene chloride and subsequent distillation at 67-68° (0.3 mm.) resulted in isolation of the colorless 2,2-dimethylthietene 1,1-dioxide (IV) in 81% conversion. Compound IV solidified on standing and could be recrystallized with some difficulty from *n*-hexane and ether, m.p. 41-42 as white hygroscopic crystals. *Anal.* Calcd. for $C_5H_8SO_2$: C, 45.45; H, 6.10; S, 24.11; M.W., 132.1. Found: C, 45.63; H, 6.40; S, 24.14; M.W., 137.3 (Osmometer in $CHCl_3$).

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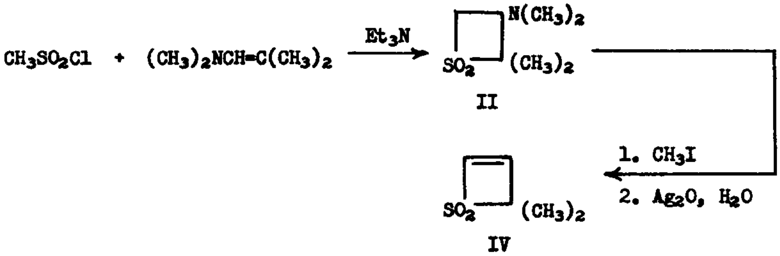
[6] K. C. Brannock, A. Bell, R. D. Burpitt, and C. S. Kelly, *J. Org. Chem.*, *26*, 625 (1961). By employing a modification of the method described by E. P. Blanchard, *J. Org. Chem.*, 28, 1397 (1963) the enamine was obtained in 45% yield, thus circumventing the need for autogenous conditions as set forth by Brannock, et al.

In addition to rapid decolorization of a dilute potassium permanganate solution, IV exhibited an infrared spectrum ($CHCl_3$) similar to thietene 1,1-dioxide[7] (I) with the characteristic weak olefinic band at 6.02 μ and strong absorbance at 7.70 μ and 8.92 μ indicative of the sulfone group. The n.m.r. spectrum[8] confirmed the structure in that two pairs of doublets (^{J}cps 4.0) were observed, one at 7.04 δ and the other at 6.65 δ in equal ratios and representative of the olefinic protons. The *gem*-dimethyl protons appeared as a strong singlet at 1.63 δ with a relative ratio of 6. The chemical shifts corresponded closely to the spectrum of I.[9]



Attempts to form thietene dioxides by amine oxide pyrolyses or by use of enamines, derived from piperidine, have to date given poor and erratic results. Further investigations are being pursued concerning the scope and limitations of this approach to thietene dioxides.

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[7] M. E. Christy, Ph.D. thesis, University of Pennsylvania, 1961.

[8] Run on a Varian A-60 spectrometer in $CDCl_3$ with TMS as an internal standard.

[9] N. S. Bhacca, L. F. Johnson, and J. N. Shoolery, "NMR Spectra Catalog", Varian Associates, Spectrum No. 22, 1962.