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A FACILE RING CLEAVAGE OF 3-AMINOTHIETANE DIOXIDES

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The pronounced ability of sulfenes to add to electron-rich olefins by means of a cycloaddition pathway is now a well known phenomenon.[1] In particular, the addition of sulfenes to enamines has provided a valuable synthetic entry to 3-aminothietane dioxides.[2] Such molecules, in contrast to 3-aminocyclobutanones,[3] are stable and have proven to be key intermediates in the synthesis of various thiete sulfones.[4] We wish to report preliminary results on a group of such compounds in which the proper disposition of a second substituent on the four-membered ring results in an extremely facile ring cleavage reaction.

Addition of two equivalents of methanesulfonyl chloride to a cold (-20°) tetrahydrofuran solution of N,N,N',N'-tetramethylpropene-1,3-diamine (1)[5] and triethylamine gave a dark oil which when chromatographed on Florisil yielded in addition to the sulfonamide 2, m.p. 49°,[6] the vinylogous sulfonamides 3, m.p. 75-6°, and 4, m.p. 69-70° (underlined atoms are those arising from the sulfene).[7] The structure of 3 followed from its infrared and n.m.r. spectra, and from its catalytic hydrogena-

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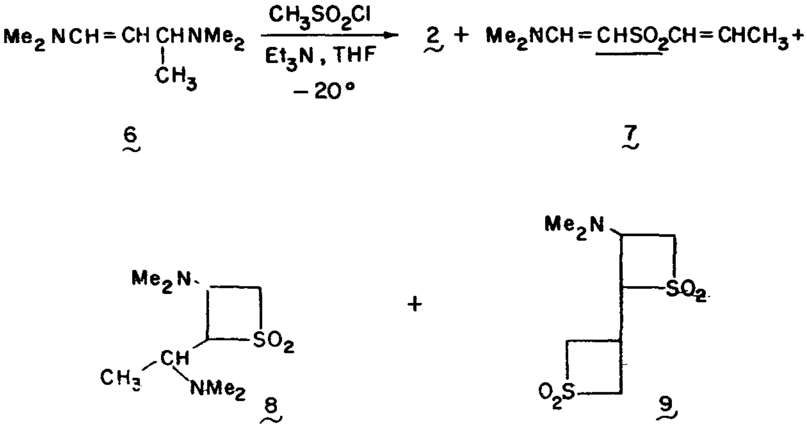
$$\underset{\mathbf{1}}{\mathrm{Me_2NCH{=}CHCH_2NMe_2}} \xrightarrow[\mathrm{Et_3N,\ THF}\ -20^{\circ}]{\mathrm{CH_3SO_2Cl}} \underset{\mathbf{2}}{\mathrm{CH_3SO_2NMe_2}} +$$

$$\underset{\mathbf{3}}{\mathrm{Me_2NCH{=}\underline{CHSO_2}CH{=}CH_2}} + \underset{\mathbf{4}}{\mathrm{Me_2NCH{=}\underline{CHSO_2}CH_2CH_2NMe_2}}$$

tion (10% Pd-C, THF) to 1-dimethylamino-3-thiapentane 3,3-dioxide (5).[8] Michael addition of dimethylamine to 3 readily yielded 4, thus interrelating the two compounds.[9]

A similar reaction of N,N,N',N'-tetramethyl-1-butene-1,3-diamine (6)[5,10] with sulfene led to a greater variety of products. There was obtained, in addition to 2 and the vinylogous sulfonamide 7, m.p. 58°,[7] the cycloaddition product 8, m.p. 38°,[7] and the interesting bithietane tetroxide 9, m.p. 148-150° (dec.).[7] Confirmation of the structure of 7 was

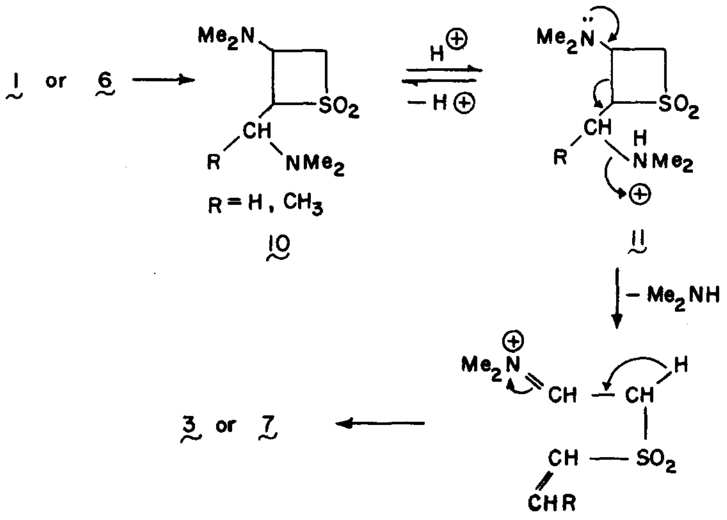


$$\underset{\mathbf{6}}{\mathrm{Me_2NCH{=}CH\underset{\displaystyle CH_3}{\underset{|}{C}}HNMe_2}} \xrightarrow[\mathrm{Et_3N,\ THF}\ -20^{\circ}]{\mathrm{CH_3SO_2Cl}} \mathbf{2} + \underset{\mathbf{7}}{\mathrm{Me_2NCH{=}\underline{CHSO_2}CH{=}CHCH_3}} +$$

achieved in a manner paralleling that employed above for **3**. The cycloadduct **8** was readily identified from its n.m.r. spectrum (in $CDCl_3$): δ 1.12 (3H, doublet, J = 7 c.p.s., CH-$\underline{CH_3}$), 2.27 and 2.32 (12H, two singlets, both NMe_2), *ca.* 3.21 (2H, multiplet, both >$\underline{CH}$-N<), and *ca.* 4.08 (3H, multiplet, $\underline{\alpha}$-sulfonyl protons). Structure **9** has been assigned on the basis of its n.m.r. spectrum which displays no vinyl protons and but one upfield proton (complex multiplet), and by its subsequent degradation.[11]

The proposed course of these interesting transformations is summarized in the Chart. The sequence of events is triggered by the expected

Chart



cycloaddition of the elements of sulfene to enamines 1 and 6 to afford 10 which serves as the key intermediate. Reversible protonation of 10 at the amino group indicated (an ample source of protons is generated in the medium by the elimination of HCl from the methanesulfonyl chloride) serves to provide an electron-deficient center which can apparently be readily ejected (as dimethylamine) by a migration of electrons from the 3-amino substituent with synchronous rupture of the four-membered ring as illustrated.

Evidence confirming this mechanistic picture was obtained from the observation that when 8 was resubmitted to the original reaction conditions, 2 and 7 were readily isolated.

Compound 4 most probably arises by Michael addition to 3 of the elements of dimethylamine shortly after its elimination and prior to the time when it is converted by excess sulfene to 2 (perhaps a solvent cage effect). Traces of a similar material from the reaction of 6 with sulfene have been observed (but not fully characterized) after extensive chromatography. The lower yield of such a Michael product in this case might be expected due to the added steric interference produced by the methyl group.

Other studies presently in progress have led us to believe that 9 arises from initial elimination of dimethylamine from enamine 6 to give 1-dimethylaminobutadiene followed by a 1,2- and 3,4-double addition of sulfene.[12]

Experiments designed to establish the breadth of this novel reaction and related transformations are currently under investigation.[13]

References

1. For recent summaries of references to the literature, see L. A. Paquette, J. Org. Chem., 29, 2851 (1964); G. Opitz, H. Schempp, and H. Adolph, Ann., 684, 92 (1965); G. Opitz and H. Schempp, ibid., 684, 103 (1965).
2. G. Stork and I. J. Borowitz, J. Am. Chem. Soc., 84, 313 (1962); G. Opitz and H. Adolph, Angew. Chem., 74, 77 (1962).
3. See, for example, G. A. Berchtold, G. R. Harvey, and G. E. Wilson, Jr., J. Org. Chem., 30, 2642 (1965).
4. W. E. Truce, J. R. Norell, J. E. Richman, and J. P. Walsh, Tetrahedron Letters, 1677 (1963); D. C. Dittmer and F. A. Davis, J. Org. Chem., 29, 3131 (1964); L. A. Paquette, ibid., 30, 629 (1965).
5. C. Mannich, K. Handke, and K. Roth, Ber., 69, 2112 (1936); see also R. C. Doss and A. M. Schnitzer, U. S. Patent 2,800,509 (July 23, 1957); Chem. Abstr., 51, 17979 (1957).
6. O. Eisleb, Ger. Patent 735,866 (April 22, 1943); Chem. Abstr., 38, 4101 (1944).
7. Satisfactory analyses were obtained for all new compounds described herein.
8. The amino sulfone 5 was characterized as its hydrochloride and perchlorate salts, m.p. 197-8° (dec.) and 92-3°, respectively. An unequivocal synthesis of 5 was achieved by oxidation of 1-dimethylamino-3-thiapentane [G. Tsatsas, C. Sandris, and D. Kontonassios, Bull. soc. chim. France, 2160 (1963)] with potassium permanganate in acetic acid.

9. In addition, **4** was catalytically hydrogenated to 1,5-bis(dimethylamino)-3-thiapentane 3,3-dioxide, characterized as its dihydrochloride, m.p. 233°. This material was identical with an authentic sample prepared by the method of W. Wieniawski [*Acta Polon. Pharm.*, **18**, 269 (1961)], m.p. 233°. We are at a loss to explain Wieniawski's reported m.p. of 248°.

10. Z. Arnold, *Coll. Czech. Chem. Comm.*, **25**, 1308 (1960).

11. This work will be described in detail in the complete paper.

12. The addition of sulfene to 1-dialkylamino-1,3-butadienes has been reported recently by G. Opitz and F. Schweinsberg [*Angew. Chem.*, **77**, 811 (1965)]. His independent work corroborates our observations.

13. Research performed under the auspices of the National Science Foundation.