Thermal Rearrangement of Thiet 1,1-Dioxide

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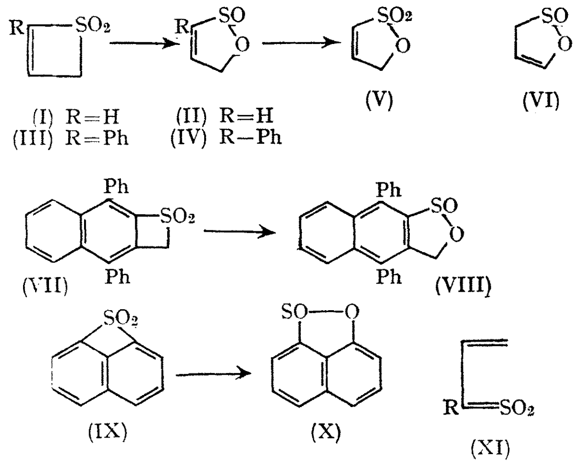
In attempts to generate sulphenes thermolytically, we heated thiet 1,1-dioxide (I) and found that it rearranges to the unsaturated cyclic sulphinic ester(II). We report work which rigorously demonstrates the course of this reaction and which suggests that a sulphene is an intermediate.

Thiet 1,1-dioxide (I), either in the vapour phase (375°, 0·002 mm., in a quartz tube) or in benzene solution (280°, 10 min.) is converted in good yield (>80%) to an oily product shown to be (II) by the following evidence. Elemental analysis and mass spectral determination of the molecular weight gave the molecular formula $C_3H_4O_2S$. The i.r. spectrum showed a strong band at 1120 cm.$^{-1}$ characteristic of a sulphinic ester,[1] and no absorption appropriate to a sulphonyl group; the n.m.r. spectrum indicated olefinic absorption *ca.* δ 7·1 and a methylene group at 5·3 and 5·7 p.p.m., J *ca.* 14 Hz. Oxidation of (II) with hydrogen peroxide in glacial acetic acid gave (V), m.p. 83—84°,[2] with i.r. bands at 1360 and 1190 cm.$^{-1}$, characteristic of a sulphonic ester. Treatment of (II) at room temperature with 1 mol. of aqueous sodium hydroxide gave an amorphous salt showing strong bands at 960 and 1020 cm.$^{-1}$ characteristic of the sulphinate anion, and no absorption assignable to an aldehyde grouping; acidification of this material regenerated the starting material (II). These observations exclude the possibility of the enol sulphinate structure (VI).

Flash thermolysis of (I) at 600° in the apparatus described in the accompanying communication[3] also led to (II). The analogous product (IV) was similarly obtained from (III), the structure following from analytical and spectroscopic data.†



(I) R=H (III) R=Ph
(II) R=H (IV) R=Ph
(V)
(VI)
(VII)
(VIII)
(IX)
(X)
(XI)

Shortly after we had discovered this reaction, Dittmer[4] made preliminary announcement of a similar rearrangement, (VII) → (VIII), and more recently rearrangement of (IX) to (X) has been reported.[5]

Both transformations have been described in terms of free-radical intermediates, but it is evident that the rearrangement of (I) and (VII) at least, can also be visualized as an electrocyclic opening of a cyclobutene-like system to give a vinylsulphene, $CH_2{=}CH{-}CR{=}SO_2$ (XI). Addition of the double bond in the "normal" way would merely give starting material, but in an "abnormal" fashion‡ would lead to the sulphinic ester.

Flash thermolysis (960°) of trimethylene sulphone, the saturated analogue of (I), gave propene (*ca.* 45%) and cyclopropane (*ca.* 50%). At lower temperatures (465—765°) no cyclic sulphinate could be detected amongst the products, though its presence would have been expected if formation of such a compound merely involved radical recombination.

In the vapour phase the reaction at 375° was unaffected by either ammonia or oxygen at pressures of 12 mm. and 30 mm. respectively. Attempts to trap a sulphene intermediate with alcohols or primary amines proved inconclusive owing either to the incursion of other reactions (*e.g.* a Mannich-type addition to the double bond) or to extensive decomposition leading to no characterized products. Reaction in a mixture of benzene and phenol (1 : 1, at 235° for 15 min.), however, led to a small yield (*ca.* 15%) of $CH_2{=}CH{\cdot}CH_2{\cdot}SO_2{\cdot}OPh$; this compound was identified by means of analysis, spectra, and independent synthesis from prop-2-ene-1-sulphonyl chloride, the latter reaction presumably proceeding *via* 1,2-addition to the sulphene as has been observed by Truce and Campbell[6] in a closely related reaction.

These observations are interpreted in terms of the sulphene (XI), most likely formed by electrocyclic opening of (I), though perhaps conceivably from bond rotation in the diradical resulting from cleavage of the 1,4-bond in (I).

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† The n.m.r. spectrum showed an ABX pattern, $\delta_A = 5{\cdot}32$, $\delta_B = 5{\cdot}72$, $\delta_X = 6{\cdot}81$ p.p.m., J_{AB} −16·0 Hz., J_{AX} 2·21 Hz., J_{BX} 1·95 Hz., together with the phenyl protons at 7·47.

‡ "Normal" and "abnormal" addition have been previously defined (T. Durst and J. F. King, *Canad. J. Chem.*, 1966, **44**, 1859) as nucleophilic attack at the sulphur and carbon atoms of the sulphene, respectively. Such abnormal attack leads to a α-substituted sulphinate anion. We suggest here a more general definition of "abnormal" nucleophilic attack as that which yields a sulphinic acid or derivative; such a definition would include nucleophilic attack on oxygen as well as on the carbon of the sulphene.

[1] L. J. Bellamy, in N. Kharasch, "Organic Sulfur Compounds", Pergamon Press, Oxford, 1961, vol. 1, p. 47.

[2] The preparation of (III) has been reported briefly: G. Manecke, J. Danhauser, and C. Reich, *Angew. Chem.*, 1958, **70**, 503; J. H. Helberger and G. Mueller, G.P. 1,146,870 (*Chem. Abs.*, 1963, **59**, 11259). These authors report m.p.'s of 78° and 83—84°, respectively.

[3] C. L. McIntosh and P. de Mayo, following Communication.

[4] D. C. Dittmer, R. S. Henion, and N. Takashina, 153rd National Meeting of the American Chemical Society, Miami, Florida, April 1967, Abstract O 101.

[5] R. W. Hoffmann and W. Sieben, *Annalen*, 1967, **703**, 96.

[6] W. E. Truce and R. W. Campbell, *J. Amer. Chem. Soc.*, 1966, **88**, 3599.