Sulphur Monoxide: Reaction with Dienes

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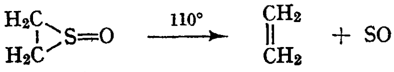
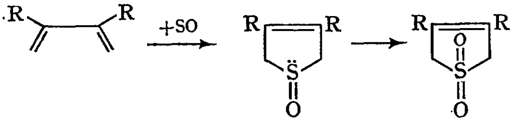
IN recent years the physical properties of sulphur monoxide have been intensively investigated.[1] However, because of the great reactivity of sulphur monoxide, very little is known about its chemical reactions, except for some knowledge of its decomposition. Recently, Hartzell and Paige[2] described the synthesis and thermal decomposition of thiiran 1-oxide (I). Controlled thermal decomposition of thiiran 1-oxide in the presence of reactive organic molecules provides a method for the controlled generation of sulphur monoxide and for the study of its chemical reactions.

Reaction of equimolar quantities of 2,3-dimethylbutadiene (II) and thiiran 1-oxide (I) in boiling toluene gave a 21% yield of 2,5-dihydro-3,4-dimethylthiophen 1-oxide[3]† (III), b.p. 67·5—69·0°/0·05 mm.; ν_{max} (neat) 1050 cm.$^{-1}$; n.m.r.‡ (CDCl$_3$) 106 (3- and 4-CH$_3$), 191, 207·5, 223·5, 240 (α-H's) c./sec. The n.m.r. resonances for the α-hydrogen atoms formed a typical AB pattern with J_{AB} = 16·5 c./sec. The bands were very broad (width at half-height as great as 6 c./sec.) indicating considerable long-range coupling. Compound (III) was oxidized with *m*-chloroperbenzoic acid to the known 2,5-dihydro-3,4-dimethylthiophen 1,1,-dioxide (IV), m.p. 133—136°. Compound (IV) was identical in all respects (m.p., mixed m.p., infrared spectrum) with an authentic sample prepared by the addition of (II) to sulphur dioxide.[4]



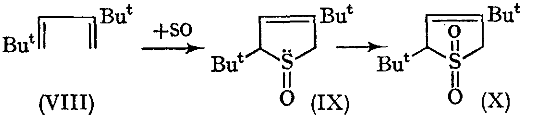
(I)



(II) R=Me
(V) R=Ph

(III) R=Me
(VI) R=Ph

(IV) R=Me
(VII) R=Ph



(VIII) (IX) (X)

Reaction of equimolar quantities of thiiran 1-oxide (I) and 2,3-diphenylbutadiene (V), and chromatography of the resulting mixture, gave 2,5-dihydro-3,4-diphenylthiophen 1-oxide (VI), m.p. 135·5—136·5° (24·7% yield), recovered (V) (35·3%), and a large number of minor products. Because of the recovery of the starting material (V), 1,3-di-t-butylbutadiene (VIII) was treated under similar conditions with the sulphur monoxide from 1·55 equivalents of thiiran 1-oxide (I). Chromatography of the products lead to the isolation of 2,5-dihydro-2,4-di-t-butylthiophen 1-oxide (IX), m.p. 85·0—86·5° (40% yield). The structures of (VI) and (IX) were established by converting them into the known dioxides, (VII) and (X)[5] respectively. Although (IX) can exist in two isomeric forms, only one sulphoxide was isolated from the reaction. Definitive evidence for the configuration of (IX) has not yet been obtained.

The ground state of sulphur monoxide is the $^3\Sigma^-$ state.[1] However, thermal decomposition of thiiran 1-oxide (I) may generate sulphur monoxide in the $^1\Sigma^+$ state (or even in the $^1\Delta$ state). The electronic state of the sulphur monoxide which reacts with the dienes to form the cyclic sulphoxides (III), (VI), and (IX) remains undefined. Questions on the electronic state of the reagent, the scope and limitations of the reactions of sulphur monoxide, and the stereochemistry and symmetry requirements of this reaction with dienes (as well as trienes) are under investigation.

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† Since it was difficult to obtain compound (III) free from traces of water (detected by infrared spectrum), analyses of it were not completely satisfactory. Analyses of compounds (VI) and (IX) were satisfactory.

‡ The n.m.r. spectra were determined with a Varian Associates A-60 spectrometer and are recorded in c./sec. downfield from tetramethylsilane.

[1] P. W. Schenk and R. Steudel, *Angew. Chem., Internat. Edn.*, 1965, **4**, 402; A. Carrington and D. H. Levy, *J. Phys. Chem.*, 1966, **71**, 5; A. Carrington, D. H. Levy, and T. A. Miller, *Proc. Roy. Soc.*, 1966, *A*, **293**, 108.

[2] G. E. Hartzell and J. N. Paige, *J. Amer. Chem. Soc.*, 1966, **88**, 2616; *J. Org. Chem.*, 1967, **32**, 459.

[3] R. C. Krug and D. E. Boswell (*J. Heterocyclic Chem.*, 1967, **4**, 309) have recently synthesized 2,5-dihydrothiophen 1-oxide by the oxidation of 2,5-dihydrothiophen.

[4] H. J. Backer and J. A. Bottema, *Rec. Trav. chim.*, 1932, **51**, 294.

[5] H. J. Backer and J. Strating, *Rec. Trav. chim.*, 1934, **53**, 525.