Sulphur Monoxide: Reaction with Trienes

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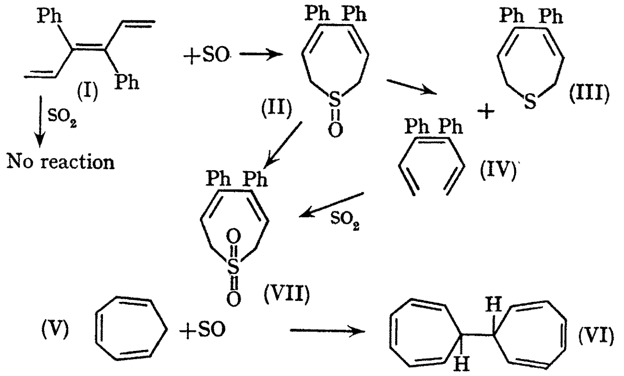
Summary Sulphur monoxide reacts with *trans*-3,4-diphenylhexa-1,3,5-triene (I) to form 2,7-dihydro-4,5-diphenylthiepin 1-oxide (II) and with cyclohepta-1,3,5-triene (V) to form dihydroheptafulvalene (ditropyl) (VI). These reactions can be understood if one assumes that sulphur monoxide reacts in the $^3\Sigma^-$ electronic state.

WE have shown[1] that the sulphur monoxide generated by the thermal decomposition of thiiran oxide reacts with dienes to produce cyclic sulphoxides. If conservation of spin is assumed, the sulphur monoxide so generated should be in the $^1\Sigma^+$ or the $^1\Delta$ electronic state. However, Saito,[2] from a study of the microwave spectrum, has been able to find only sulphur monoxide in the $^3\Sigma^-$ state among the thermal decomposition products of thiiran oxide. Here we present evidence that sulphur monoxide, generated by the thermal decomposition of thiiran oxide, may be reacting in the $^3\Sigma^-$ state with trienes.

trans-3,4-Diphenylhexa-1,3,5-triene (I),[†] m.p. 126—127°; n.m.r. ($CDCl_3$, p.p.m.): ν_A 5·04, ν_B 4·77, ν_X 6·50; J_{AB} 1·9 c./sec., J_{AX} 10·5, J_{BX} 17·3;[‡] was synthesized from propiophenone *via* the pinacol condensation[3] [Al(Hg) in ethanol: benzene], dehydration to the diene[4] (acetyl chloride), bromination of the diene, followed by dehydrohalogenation ($KOBu^t$ in dimethyl sulphoxide). Reaction of (I) with sulphur monoxide (generated by thermal decomposition of an equimolar quantity of thiiran 1-oxide) in toluene at 110°, followed by chromatography of the product on silica gel yielded 2,7-dihydro-4,5-diphenylthiepin 1-oxide (II), m.p. 162°, yield 35%; ν_{max} (Nujol) 1080, 1055 cm^{-1}; n.m.r. ($CDCl_3$, p.p.m.) 3·39, 3·41, 3·53 (4·25 H, α-H's); 6·66, 6·78, 6·91 (1·82 H, β-H's); 7·19 (9·9 H, 2-Ph). Oxidation of (II) with an equivalent quantity of *m*-chloroperbenzoic acid in chloroform gave a quantitative yield of 2,7-dihydro-4,5-diphenylthiepin 1,1-dioxide (VII), m.p. 190°; λ_{max} (ethanol) 245 nm (25,200);[5] ν_{max} (Nujol) 1320, 1309, 1132 cm^{-1}; n.m.r. ($CDCl_3$, p.p.m.) 3·79 (d, J = 7·4 c./sec., 3·73 H, α-H's), 6·50 (t, J = 7·7 c./sec., 2·03 H, β-H's); 7·20 (s, 10·24 H, 2-Ph).



Reduction of (II) with lithium aluminium hydride in ether, followed by chromatography of the products on florisil yielded 2,7-dihydro-4,5-diphenylthiepin (III), m.p. 142—143°, n.m.r. ($CDCl_3$, p.p.m.) 3·08 (d, J *ca.* 8 c./sec., 3·6 H, α-H's), 6·63 (*t*, J *ca.* 8 c./sec., 2·0 H, β-H's), 7·23 (s, 10·39 H, 2 Ph), and *cis*-3,4-diphenylhexa-1,3,5-triene (IV), n.m.r. ($CDCl_3$, p.p.m.) ν_A 5·31, ν_B 4·92, ν_X 7·26, J_{AB} 1·8 c./sec., J_{AX} 10·7, J_{BX} 17·1.[‡] The *cis*- hexatriene (IV) was identified and its stereochemistry assigned

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[†] Satisfactory analyses were obtained on the *trans*-triene (I) and on the dihydrothiepins (II, III, and VII). The *cis*-triene (IV) was obtained in too small a quantity for analysis.

[‡] N.m.r. spectra are recorded in p.p.m. downfield from tetramethylsilane. Coupling constants from calculated spectra should be accurate to 0·5 c./sec.

initially by comparison of the parameters calculated from its n.m.r. spectrum with those obtained from the n.m.r. spectrum of the *trans*-hexatriene (I). The structure and stereochemistry were confirmed by the reaction of the *cis*-hexatriene (IV) with sulphur dioxide at room temperature in chloroform to form 2,7-dihydro-4,5-diphenylthiepin 1,1-dioxide (VII).[6] Under comparable conditions or under considerably more drastic conditions of temperature and pressure the *trans*-3,4-diphenylhexa-1,3,5-triene (I) failed to react with sulphur dioxide. *trans*-3,4-Diphenylhexa-1,3,5-triene (I) was not isomerized to the *cis*-isomer (IV) when heated in toluene at 110° for 4 hours, conditions comparable to those used for its reaction with sulphur monoxide.

Reaction of cyclohepta-1,3,5-triene (V) with sulphur monoxide (generated by thermal decomposition of an equimolar amount of thiiran 1-oxide) at 110° in toluene gave dihydroheptafulvalene (ditropyl) (VI),[7] m.p. 60—61°, yield *ca.* 7%, $\lambda_{\max}$ (pentane) 252 nm (ϵ 6,740); mass spectrum,[8] M^+ m/e 182, most abundant ion m/e 91. No ditropyl (VI) was formed from cycloheptatriene (V) in a reaction run under comparable conditions but without the addition of thiiran 1-oxide.

The reaction of sulphur monoxide with *trans*-3,4-diphenylhexa-1,3,5-triene (I) indicates that sulphur monoxide can catalyze the isomerization of the *trans*-hexatriene to the *cis*-isomer, or that sulphur monoxide can react in a multiple step, non-concerted reaction with *trans*-hexatriene, or both. The formation of ditropyl (VI) from cycloheptatriene (V), when the latter is exposed to sulphur monoxide, probably results from the coupling of an intermediate radical. The above reactions can be best understood if it is assumed that sulphur monoxide reacts, at least in part, in the $^3\Sigma^-$ electronic state.

This research was supported by a fellowship from the Lubrizol Corp., Cleveland, Ohio, and in part, by the National Institutes of Health of the U.S. Public Health Service.

(*Received, June 20th*, 1969; *Com.* 890.)

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