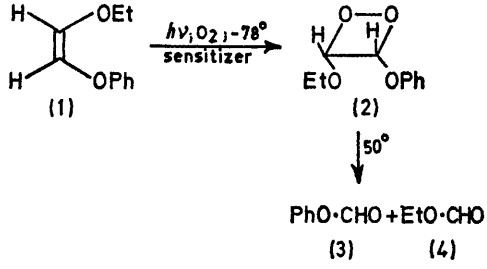
Stereochemistry of the Addition of Singlet Oxygen to Vinylene Diethers[1]

By A. PAUL SCHAAP* and NARONGSAK TONTAPANISH
(*Department of Chemistry, Wayne State University, Detroit, Michigan* 48202)

Summary The stereochemistry of the predominant mode of addition of singlet oxygen to vinylene diethers to yield 1,2-dioxetans is unequivocally established as *cis* with respect to the olefin.

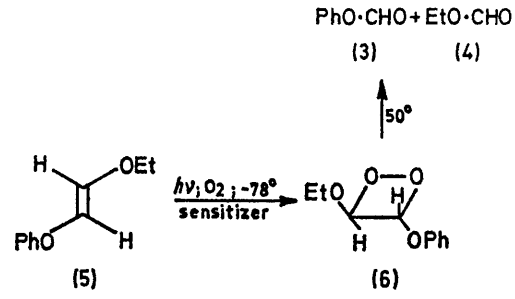
WE recently reported that singlet oxygen adds stereospecifically to *cis*- and *trans*-diethoxyethylenes to give 1,2-dioxetans,[2] probably in a *cis*-fashion with retention of the configuration of the olefin in the dioxetan. Described herein is evidence confirming the *cis*-addition of singlet oxygen to vinylene diethers.

Photo-oxidation of *cis*- and *trans*-ethoxyphenoxyethylenes (**1**) and (**5**) at −78° in trichlorofluoromethane with tetraphenylporphin sensitization gave the 1,2-dioxetans (**2**) and (**6**) respectively.† The vinylene diethers were synthesized as a mixture of (**1**) and (**5**) (95:5) from the vapour-phase reaction at 250° of 1,1-diethoxy-2-phenoxyethane with activated alumina,[3] and purified by preparative g.l.c. The photo-oxidations were followed by n.m.r. spectroscopy.



The configurations of the dioxetans were assigned on the basis of n.m.r. vicinal coupling constants [n.m.r. data: (**2**) δ ($CFCl_3$) 1·30 (3H, t, *J* 7·0 Hz), 4·01 (2H, q, *J* 7·0 Hz), 6·07 (1H, d, *J* 3·9 Hz), 6·35 (1H, d, *J* 3·9 Hz), and 7·08 (5H, s) p.p.m.; (**6**) δ ($CFCl_3$) 1·30 (3H, t, *J* 7·0 Hz), 3·77 (2H, q, *J* 7·0 Hz), 5·89 (1H, d, *J* 3·2 Hz), 6·12 (1H, d, *J* 3·2 Hz), and 7·10 (5H, s) p.p.m.]. The low-field AB quartets at δ 6·07 and 6·35 for (**2**) and δ 5·89 and 6·12 for (**6**) have coupling constants of 3·9 and 3·2 Hz respectively. Assuming that the dihedral angles involved are approximately equal to those for carbocyclic analogues (*cis* 0°; *trans* 127°),[4] the Karplus equation predicts that the *cis*-dioxetan should exhibit a larger coupling constant than the *trans*.[5] The assignments are strongly supported by n.m.r. data for several model oxetans, for which the *cis*-vicinal coupling constants are larger than the *trans* by 1·0–0·6 Hz.[4,6]

(**2**) and (**6**) are relatively stable at ambient temperature, but decompose quantitatively to (**3**) and (**4**) (identical with authentic samples) on brief heating to 50—70°.[7] Chemiluminescence occurs in these decompositions in the presence of 9,10-dibromoanthracene.[8]



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† Photo-oxidation of (**1**) results in stereospecific formation of (**2**) whereas (**5**) yielded irreproducible mixtures of (**6**) (90—75%) and (**2**) (10—25%). This lack of stereospecificity in the photo-oxidation of (**5**) is under investigation.

[1] Presented at the Symposium on Oxidation by Singlet Oxygen, 162nd National Meeting of the American Chemical Society, Washington, DC, September 15th, 1971.

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