

(therefore 90% D). If we assume, reasonably, that the d_2 and d_3 species contain one of their deuteriums at C-3, the total at C-3 should be 91% D (i.e., $86 + 4 + 1$), which agrees closely with the nmr integration.¹⁵

The ready bridgehead exchange in brendan-2-one is not paralleled in its bicyclic analog, bicyclo[3.2.1]octan-2-one (**8**), in which the ketonic ring is conformationally more flexible. Thus ketone **8** exchanged virtually only its two enolizable protons (3% d_0 , 24% d_1 , 72% d_2 , 1% d_3), when treated with NaOCH₃ under the conditions of run 3, Table I. Use of KO-*t*-Bu-*t*-BuOD at 40° gave closely similar incorporation, and, even at 170° with KOD in 1:1 D₂O-dioxane, the recovered ketone showed very little uptake beyond d_2 (0% d_0 , 10% d_1 , 87% d_2 , 2% d_3 , 1% d_4).¹⁶

The unusual ease of bridgehead replacement in **3** and its relative difficulty in **7** and **8** demonstrate that the bridged boat form markedly enhances enolate stability at the side of the boat (but not at the bow) and that this stabilization is diminished considerably in a locked chair form. Our results imply that boat-locked substrates might be used to advantage in pursuit of certain anti-Bredt olefins.¹⁷ The findings also raise the interesting possibility that prior to enolization of equatorial hydrogens, ordinary cyclohexanones may prefer to change to boat-like shapes to improve initial stereoelectronic alignment. We are pursuing some of these suggested lines.

References and Notes

- (1) Supported by the National Institutes of Health (Grant GM06304) and by the National Science Foundation.
- (2) K. W. Turnbull, S. J. Gould, and D. Arigoni, *J. Chem. Soc., Chem. Commun.*, 597 (1972).
- (3) D. H. Bowen and J. MacMillan, *Tetrahedron Lett.*, 4111 (1972).
- (4) A. Nickon, H. Kwasnik, T. Swartz, R. O. Williams, and J. B. DiGiorgio, *J. Am. Chem. Soc.*, **87**, 1615 (1965).
- (5) All proton signals in natural abundance ketone were readily assigned with the aid of spin-decoupling in a spectrum shifted by Eu(fod)₃. Details, including coupling constants, are described by D. Covey, Ph.D. Dissertation, The Johns Hopkins University, 1973.
- (6) (a) P. G. Gassman and F. V. Zalar, *J. Am. Chem. Soc.*, **88**, 3070 (1966); (b) P. T. Lansbury and J. D. Sidler, *Tetrahedron Lett.*, 691 (1965).
- (7) A. Nickon and J. L. Lambert, *J. Am. Chem. Soc.*, **88**, 1905 (1966).
- (8) For recent reviews on Bredt's rule, see G. Köbrich, *Angew. Chem., Int., Ed. Engl.*, **12**, 464 (1973); G. L. Buchanan, *Chem. Soc. Rev.*, **3**, 41 (1974).
- (9) (a) J. R. Wiseman, *J. Am. Chem. Soc.*, **89**, 5966 (1967); (b) J. R. Wiseman and W. A. Fletcher, *ibid.*, **92**, 956 (1970).
- (10) A. Nickon, G. D. Pandit, and R. O. Williams, *Tetrahedron Lett.*, 2851 (1967).
- (11) Boat-shapes have been suggested for bridgehead enolization (J. P. Shafer and J. C. Lark, *J. Org. Chem.*, **30**, 1337 (1965) and decarboxylative-elimination (J. A. Marshall and H. Faubl, *J. Am. Chem. Soc.*, **89**, 5965 (1967)) in bicyclo[3.3.1]nonane systems.
- (12) In sulfones containing a bicyclo[3.3.1]nonane skeleton strong evidence exists for transient formation of isomeric *cis*- and *trans*-cyclohexenes. C. B. Quinn, J. R. Wiseman, and J. C. Calabrese, *J. Am. Chem. Soc.*, **95**, 6121 (1973).
- (13) A. Nickon and J. L. Lambert, *J. Am. Chem. Soc.*, **84**, 4604 (1962); A. Nickon, J. L. Lambert, R. O. Williams, and N. H. Werstliuk, *ibid.*, **88**, 3354 (1966), and references cited.
- (14) The higher homolog adamantan-2-one, which also has a chair-locked cyclohexanone, is reported to be very resistant to exchange. J. E. Nordlander, S. P. Jindal, and D. J. Kitko, *Chem. Commun.*, 1136 (1969). In our own studies with adamantanone, we found only 8% d_1 after 192 hr in *t*-BuOD-KO-*t*-Bu at 195°, and at higher temperature (205°) the exchange produced d_1 , d_2 , and d_3 species due to bridgehead and homoenolate abstraction. J. B. Stothers and C. T. Tan (private communication) independently observed exchange in adamantan-2-one and also established that the relative ease of replacement is $4\text{-H}_{\text{exo}} > 1\text{-H} > 4\text{-H}_{\text{endo}}$.
- (15) The bridgehead hydrogens at C-3 and C-1 are not geometrically identical because of some distortion in the chair. For computer calculation on noradamantane geometry see E. M. Engler, J. D. Androse, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8005 (1973).
- (16) Similar results were obtained at room temperature with NaOD in MeOD by R. T. Lalonde, J. Ding, and M. A. Tobias, *J. Am. Chem. Soc.*, **89**, 6651 (1967).
- (17) J. A. Chong and J. R. Wiseman, *J. Am. Chem. Soc.*, **94**, 8627 (1972).

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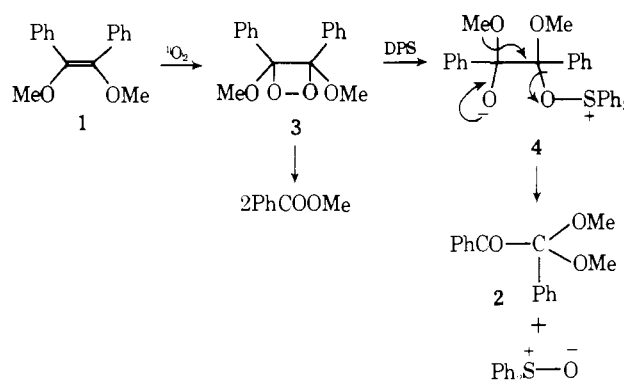
Trapping of Intermediates in Singlet Oxygen Reactions. Cleavage of Dioxetanes by Diphenyl Sulfide

Sir:

Recent investigations on the mechanisms of singlet oxygen reactions with acceptors have made use of various trapping agents to intercept peroxidic intermediates.¹⁻⁴ Among these, diphenyl sulfide (a species unreactive toward ¹O₂) has been used effectively to bring about monodeoxygenation of persulfoxides formed in the sensitized photooxidation of alkyl sulfides.¹ We now report that diphenyl sulfide (DPS) may be used as a trapping agent to intercept dioxetanes formed in the reactions of singlet oxygen with certain electron-rich ethylenic and heterocyclic systems.

Methylene Blue-sensitized photooxidation of *cis*-dimethoxystilbene (**1**) (625-W Sylvania "Sun Gun") (0.005 *M*) in ether-methanol (85:15) in the presence of excess DPS (0.02 *M*) yielded methyl benzoate (32%) benzil dimethyl ketal (**2**)⁵ (18%), and diphenyl sulfoxide (35%).⁶ In the absence of DPS, we have found as has been reported earlier,^{7,9} that reaction of **1** with singlet oxygen under the same conditions yields only the dioxetane (**3**) and its cleavage product, methyl benzoate.

We suggest that the formation of the rearrangement product (**2**), in the presence of DPS, takes place by a nucleophilic attack of the sulfide on the intermediate dioxetane (**3**) with cleavage of the oxygen-oxygen bond.⁸ The zwitterion (**4**) thus formed then undergoes a benzylic acid-like rearrangement as shown.^{10,11} This explanation receives strong support from a control experiment in which the dioxetane (**3**), isolated in pure form,⁹ was treated with DPS at room temperature in ether-CD₃OD. The resulting mixture of products contained **2** (21%), diphenyl sulfoxide (32%), and methyl benzoate (43%). No incorporation of OCD₃ from the solvent was observed. In benzene, **3** reacted at a much slower rate with DPS to give the same products.



The effect of DPS on the photosensitized oxygenation of 2,3-diphenyl-*p*-dioxene (**5**) was next investigated. In the absence of trapping agent, this oxidation yields the 1,2-dioxetane (**6**) which cleaves to form the dibenzoate of ethylene glycol (**7**).^{7,12} Photooxidation of **5** (0.02 *M*) in moist methanol (Methylene Blue) in the presence of DPS (0.16 *M*) yielded the *trans*-glycol **8**^{13,14} (40%) and diphenyl sulfoxide (47%) along with the cleavage product **7** (18%). As the concentration of DPS was increased the ratio of **7** to **8** markedly decreased, as shown in Table I.²⁶ Using benzene as solvent, bisacacenaphthalenethiophene as sensitizer, and DPS (0.05 *M*) as oxygen scavenger, the products formed were benzil ethylene ketal (**9**) (8%), epoxide (**10**) (19%), **7** (24%), and diphenyl sulfoxide (39%). Formation of products **8**, **9**, and **10** is shown in Scheme I.^{14,27}

Diphenyl sulfide does not cause monodeoxygenation of

Scheme 1

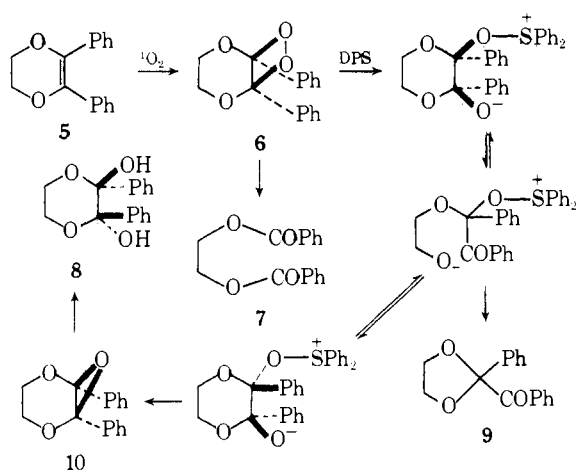


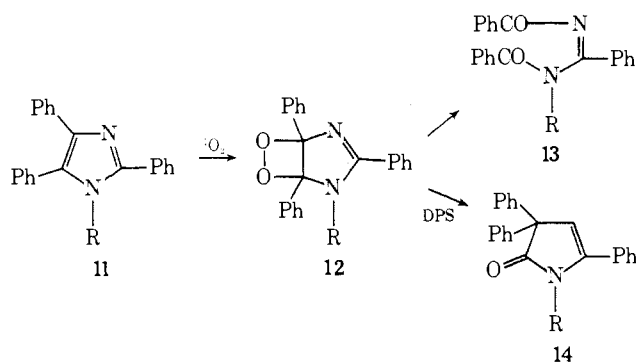
Table I. Variation of the Product Ratio (7:8) with Concentration of Diphenyl Sulfide (DPS)

5 (M)	DPS (M)	Ratio of 7:8 ^a
0.01	0.04	1.20
0.01	0.08	0.65
0.01	0.10	0.52

^a Determined by nmr analysis of the reaction mixture.

intermediates in the dye-sensitized photooxidation of tetraphenylcyclopentadienone, 2,5-diphenyl-4-methyloxazole, 9,10-diphenylanthracene, 2,3-dimethylthiophene, or 2-methylfuran, where the products formed are virtually the same with or without DPS, and *no* diphenyl sulfoxide is observed. These findings are consistent with the fact that dioxetanes have not been found to be intermediates in any of the above singlet oxygen reactions which are generally considered¹⁵ to involve 1,4-transannular peroxides. We have independently found that DPS is inert to 9,10-diphenylanthracene peroxide, ascaridole, and 1,4-dimethylnaphthalene 1,4-endoperoxide¹⁶ among other 1,4-transannular peroxides. We have also observed that dye-sensitized photooxidation of tetramethylethylene in the presence of a 4 M excess of DPS gave only allylic hydroperoxide, the typical "ene" product, and no diphenyl sulfoxide.

On the other hand, the presence of DPS has a marked effect on the oxidations of the tetrasubstituted imidazoles **11a** and **11b** which normally undergo facile C₄-C₅ ring cleavage with singlet oxygen through intermediates generally considered to be dioxetanes.¹⁷⁻¹⁹ Thus, photooxidation of tetraphenylimidazole (**11a**) in benzene-acetone (9:1) (Methylene Blue) yielded the rearrangement product (**14**) (33%) and diphenyl sulfoxide (41%) in addition to the usual cleav-



a, R = Ph
b, R = CH₂Ph

age product (**13**) (12%). In the absence of DPS the dibenzoyl derivative (**13**) was obtained in nearly quantitative yield, as reported earlier.¹⁷ Similar results were observed in the photooxidation of **11b**. As in the cases cited above, reaction of DPS with the intermediate dioxetanes (**12**) would lead to the observed rearrangement.

Along with certain dioxetanes²⁰ and persulfonides, it appears that carbonyl oxides, postulated as intermediates in singlet oxygen reactions,²³⁻²⁵ may also undergo DPS mono-deoxygenation. Thus, we have found that the dye-sensitized photooxidation of diphenyldiazomethane in the presence of DPS yields only benzophenone and diphenyl sulfoxide and none of the (dimeric) tetroxide normally observed.

References and Notes

- C. S. Foote and J. W. Peters, *J. Am. Chem. Soc.*, **93**, 3795 (1971).
- (a) W. Fenical, D. R. Kearns, and P. Radlick, *J. Am. Chem. Soc.*, **91**, 7771 (1969); (b) N. M. Hasty, P. B. Merkel, P. Radlick, and D. R. Kearns, *Tetrahedron Lett.*, 49 (1972); (c) C. S. Foote, T. T. Fujimoto, and Y. C. Chang, *ibid.*, 45 (1972).
- N. M. Hasty and D. R. Kearns, *J. Am. Chem. Soc.*, **95**, 3380 (1973).
- A. P. Schaap and G. R. Faler, *J. Am. Chem. Soc.*, **95**, 3381 (1973).
- R. Kuhn and H. Trishman, *Chem. Ber.*, **94**, 2258 (1961).
- Yields of products in experiments reported here are isolated yields after column chromatography and preparative tic separation. In all cases polymeric products were detected during chromatographic separation.
- P. D. Bartlett, G. D. Mendenhall, and A. P. Schaap, *Ann. N. Y. Acad. Sci.*, **171**, 79 (1970).
- A similar type of cleavage reaction of tetramethyl-1,2-dioxetane has been reported recently. P. D. Bartlett, A. L. Baumstark, M. E. Landis, and C. L. Lerman, *J. Am. Chem. Soc.*, **96**, 5267 (1974); P. D. Bartlett, A. L. Baumstark, and M. E. Landis, *ibid.*, **96**, 5557 (1974).
- G. Rio, J. Berthelet, *Bull. Soc. Chim. Fr.*, 3555 (1971).
- Analogous rearrangements have been reported earlier, as in the reaction of tetraphenylpyrrole with singlet oxygen in the presence of base: (a) H. H. Wasserman and A. Liberles, *J. Am. Chem. Soc.*, **82**, 2086 (1960); (b) C. Dufraisse, G. Rio, and A. Ranjon, *C. R. Acad. Sci.*, **246**, 1337 (1958).
- W. Ando, J. Suzuki, T. Arai, and T. Migita, *Tetrahedron*, **29**, 1507 (1973), have observed a related migration of a thioethyl group in the reaction of singlet oxygen with bis(ethylthio)ethylene, presumably by formation of an intermediate dioxetane which is then attacked by sulfide.
- A. P. Schaap, *Tetrahedron Lett.*, 1757 (1971).
- Satisfactory elemental analyses were obtained for new compounds except the epoxide (**10**), which was very readily hydrolyzed under the usual isolation conditions and characterized by conversion to **8** in aqueous methanol.
- Compound **8** shows the expected ir, nmr, and mass spectroscopic data. It was prepared independently either by oxidation of **5** with performic acid or by dissolving the epoxide (**10**) in moist methanol.
- (a) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968); (b) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971); (c) W. R. Adams in "Oxidation," Vol. 2, R. L. Augustine and D. J. Trecker, Ed., Marcel Dekker, New York, N. Y., 1971, p 65.
- H. H. Wasserman and D. L. Larsen, *J. Chem. Soc., Chem. Commun.*, 253 (1973).
- H. H. Wasserman, K. Stiller, and M. B. Floyd, *Tetrahedron Lett.*, 3277 (1968).
- A. Ranjon and M. C. Dufraisse, *C. R. Acad. Sci., Ser. C*, **267**, 1822 (1968), have shown that the photooxidation of **11a** at -60° gives an unstable peroxide considered to be a dioxetane, but the structure of this peroxide has not yet been established.
- M. L. Wolf, Ph.D. Dissertation, Yale University, 1971.
- We have found that although singlet oxygen reactions with enamines appear to take place through dioxetane intermediates, oxidations of enamines such as *N,N*-diethylisobutenylamine²¹ or *N*-methyltetrahydrocarbazole²² are not affected by DPS. We are seeking an explanation for this anomaly.
- C. S. Foote and J. W. P. Lin, *Tetrahedron Lett.*, 3267 (1968).
- I. Saito, M. Imuta, and T. Matsuura, *Chem. Lett.*, 1197 (1972).
- H. H. Wasserman and A. Miller, *Chem. Commun.*, 199 (1968).
- P. D. Bartlett and J. G. Traylor, *J. Am. Chem. Soc.*, **84**, 3408 (1962).
- (a) R. W. Murray and A. Suzui, *J. Am. Chem. Soc.*, **95**, 3343 (1973); (b) D. P. Higley and R. W. Murray, *ibid.*, **96**, 3330 (1974).
- The reaction of *p*-dioxene with singlet oxygen in moist methanol in the presence of DPS yielded dioxane-2,3-diol (19%) in addition to $O=CHO-CH_2CH_2OC(H)=O$ (22%). The diformate is formed exclusively in the same reaction without DPS.
- The formation of **10** (and **8**) could, of course, also result from mono-deoxygenation of a peroxirane intermediate^{24,28} formed as a precursor to the dioxetane.
- D. R. Kearns, W. Fenical, and P. Radlick, *Ann. N. Y. Acad. Sci.*, **171**, 34 (1970).

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