$EtC(CH_2O)_3P{\cdot}O_3$: a Relatively Stable Bicyclic Phosphite–Ozone Adduct and a Convenient Singlet Oxygen Source

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Summary The bicyclic phosphite 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane readily forms an ozone adduct of striking stability which efficiently produces singlet oxygen at temperatures above 0°.

RECENTLY, multiple methods for singlet oxygen generation, and the subsequent use of this ubiquitous reagent in chemical oxygenations have received considerable attention.[1] A particularly convenient procedure employs the well known triphenyl phosphite–ozone adduct[2] at $> -35°$ to accomplish singlet oxygen oxidations both in solution and in the gas phase.[1] Only the triaryl phosphites give stable ozone adducts[2] at $-78°$, although triethyl phosphite ozonide has recently been reported to have limited stability at $-95°$.[1]

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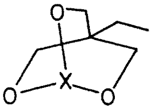
We now report that the bridged, bicyclic phosphite (I) forms an ozone adduct (III) which is significantly *more stable* than $(PhO)_3P{\cdot}O_3$ and which is an excellent preparative source of singlet oxygen at temperatures above 0°.



(I) X = P
(II) X = PO
(III) X = PO_3

Dilute[1,2] CH_2Cl_2 solutions ($<$ 0·06M) of 4-ethyl-2,6,7-trioxa-1-phosphabicyclo[2,2,2]octane (I)‡ react[3] quantitatively at $-78°$ with one equivalent of ozone (O_3–O_2) to give an ozone adduct (III), which after nitrogen purging and subsequent warming to room temperature, affords nearly a quantitative yield of the corresponding phosphate (II), m.p. 205—206° (lit.[3] 207—208°), i.r., P=O at 7·53s μm (lit.[4] 7·55), in addition to the evolution of *ca.* 1 equivalent of oxygen.§

Evidence that thermal decomposition of (III) produces singlet oxygen was provided by the usual[1] trapping experiments at $-78°$, followed by slow warming to room temperature.[5] In this way tetraphenylcyclopentadienone gave a 28% isolated yield of *cis*-dibenzoylstilbene, m.p. 212—213° (lit.[6] 216—217°) and i.r. spectrum identical to that reported (ref. 6); 9,10-diphenylanthracene gave a 86% isolated yield of the corresponding *endo*-peroxide, decomp. 176° (lit.[1,7] *ca.* 200°; 180°) with vigorous gas evolution and regeneration of 9,10-diphenylanthracene. Yields, employing $(PhO)_3$-$P{\cdot}O_3$, are reported to be 36·6% and 77%, respectively.[1] It should be noted that phosphate (II) is completely insoluble in solvents such as benzene thus allowing for a relatively simple product separation and purification scheme.

Preliminary kinetic studies (*via* oxygen evolution) at 10° reveal that bicyclic phosphite–ozone adduct (III) undergoes decomposition by a first order reaction with $k = 9{\cdot}10 \times 10^{-3}$ min^{-1} and $t_{\frac{1}{2}} = 76{\cdot}2$ min. Extrapolation of the reported[1] kinetic data for $(PhO)_3P{\cdot}O_3$ to 10° gives $k = 1{\cdot}47$ min^{-1} and $t_{\frac{1}{2}} = 0{\cdot}47$ min. Thus the adduct (III) exhibits remarkable stability, especially when compared to the fleeting existence of $(EtO)_3P{\cdot}O_3$ at $-95°$, and is in fact $>$ 160 times more stable than $(PhO)_3P{\cdot}O_3$ at 10°. This is tentatively attributed to the unique, symmetrical, relatively strain-free, bicyclic system of fixed and rigid geometry, which apparently influences the stability of (III) by a favourable entropy effect.[8] Furthermore, the above results suggest that other similar polycyclic phosphites, such as 2,8,9-trioxa-1-phospha-adamantane,[9] may well form ozone adducts of even greater stability than (III). Polycyclics containing arsenic, sulphur, *etc.* may also be of considerable interest in the ozone adduction reaction.

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§ In the convenient diagnostic test for singlet oxygen (rubrene bleaching), ref. 1 reports slight colour loss at $-35°$, colourless at $-25°$, and vigorous gas evolution at $-10°$ for $(PhO)_3P{\cdot}O_3$. With adduct (III) we observe the same phenomena at 12°, 14°, and 22° respectively.

[1] For a summary, see R. W. Murray and M. L. Kaplan, *J. Amer. Chem. Soc.*, 1969, **91**, 5358 and references cited therein.

[2] W. S. Knowles and Q. E. Thompson, *Chem. and Ind.*, 1959, 121; Q. E. Thompson, *J. Amer. Chem. Soc.*, 1961, **83**, 846.

[3] W.-H. Chang, *J. Org. Chem.*, 1964, **29**, 3711; W.-H. Chang and M. Wismer, U.S. Pat. 3,189,633/1965 have reported instant ozone oxidation of (I) and related phosphites at room temperature.

[4] J. G. Verkade and L. T. Reynolds, *J. Org. Chem.*, 1960, **25**, 663.

[5] A bimolecular reaction between (III) and the acceptors at $-78°$ was not observed; *i.e.*, no colour change apparent until $>$10°. *Cf.* P. D. Bartlett and G. D. Mendenhall, *J. Amer. Chem. Soc.*, 1970, **92**, 210.

[6] D. R. Burger and R. K. Summerbell, *J. Org. Chem.*, 1959, **24**, 1881.

[7] C. Dufraisse and J. LeBras, *Bull. Soc. chim. France*, 1937, **4**(5), 349.

[8] See R. D. Bertrand, R. D. Compton, and J. G. Verkade, *J. Amer. Chem. Soc.*, 1970, **92**, 2702 and earlier papers for work on structural considerations of a variety of dipolar heteropolycyclics.

[9] J. G. Verkade, T. Hutteman, M. Fung, and R. W. King, *Inorg. Chem.*, 1965, **4**, 83.