$EtC(CH_2O)_3P \cdot O_3$: 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-1phosphabicyclo[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 adduct² at > -35° to accomplish singlet oxygen oxidations both in solution and in the gas phase.¹ Only the triaryl phosphites give stable ozone adducts² 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 $(PhO)_{3}P \cdot O_{3}$ and which is an excellent preparative source of singlet oxygen at temperatures above 0° .

$$(I) X = P$$

$$(I) X = PO$$

$$(I) X = PO$$

$$(II) X = PO_3$$

Dilute^{1,2} CH_2Cl_2 solutions (< 0.06M) of 4-ethyl-2,6,7trioxa-1-phosphabicyclo[2,2,2]octane (I)⁺₊ react³ quantitatively at -78° with one equivalent of ozone (O₃-O₂) 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 μ m (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 usual¹ 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 = 9.10 \times 10⁻³ min⁻¹ and $t_{\frac{1}{2}} =$ 76.2 min. Extrapolation of the reported¹ kinetic data for (PhO)₃P·O₃ to 10° gives k = 1.47min⁻¹ and $t_{\frac{1}{2}} = 0.47$ 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·O₃. 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.
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⁷ C. Dufraisse and J. LeBras, Bull. Soc. chim. France, 1937, 4(5), 349.
⁸ See R. D. Berterrod, R. D. Ormeton and L. C. Verlede, L. Amer. Chem. See, 1070, 92, 2709 and earlier ensure for much an etric.

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