

catalytic point of view is the axial lability of Fe(II)TPPS, which provides the release of bound ammonia following its formation and the subsequent reentry of Fe(II)TPPS into the nitrite reduction cycle.

As a last point, it is important to note that the active site in the nitrite reductase enzymes¹² is thought to be based on an iron heme unit. The results reported here may provide mechanistic insight into the chemical details of the operation of this enzyme system.

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Registry No. 1, 58452-44-1; 2, 83006-31-9; 3, 78913-50-5; *cis*-[Ru(bpy)₂(NO)Cl]²⁺, 31847-83-3; *cis*-[Ru(bpy)₂(NH₃)(H₂O)]²⁺, 83006-32-0; *cis*-[Ru(bpy)₂(NO)py]³⁺, 47713-31-5; *cis*-[Ru(bpy)₂(NH₃)py]²⁺, 83006-33-1; [Os(trpy)(bpy)NO]³⁺, 83006-34-2; [Os(trpy)(bpy)NH₃]²⁺, 83006-35-3; *cis*-[Ru(bpy)₂(NO)(NO₂)]²⁺, 47637-63-8; *cis*-[Ru(bpy)₂(NH₃)₂]²⁺, 56993-98-7; Fe(II)TPPS, 83006-36-4; NO₂⁻, 14797-65-0; NH₃, 7664-41-7; nitrite reductase, 9080-03-9.

(12) Murphy, M. J.; Siegel, L.; Tove, S.; Kamin, H. *Proc. Natl. Acad. Sci. U.S.A.* 1974, 71, 612.

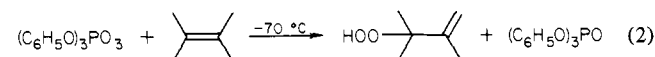
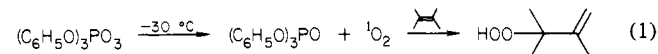
Transfer of O₂ from Triphenyl Phosphite Ozonide to Alkyl-Substituted Olefins

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Two general mechanisms have been recognized for phosphite ozonide reactions with olefins. In the first of these, the ozonide decomposes to phosphate and singlet oxygen¹ followed by normal singlet oxygen reactions (reaction 1). At temperatures lower than those required for this unimolecular decomposition, one can frequently observe a direct bimolecular reaction² between ozonide and olefin that results in the delivery of O₂ to the olefin (reaction 2).



Results from Bartlett's laboratory^{2b,c,3} make it clear that the mechanistic details of pathways 1 and 2 can differ dramatically. With the vinyl ethers below, Bartlett and co-workers favor a [2 + 2]cycloaddition pathway³ for the singlet oxygen reaction (reaction 3) and a two-step pathway^{2b,c} with a long-lived zwitterionic intermediate in the direct reaction (reaction 4). We point out in this communication that the direct reaction of phosphite ozonides with tetramethylethylenes is, in contrast, very similar to that of singlet oxygen.

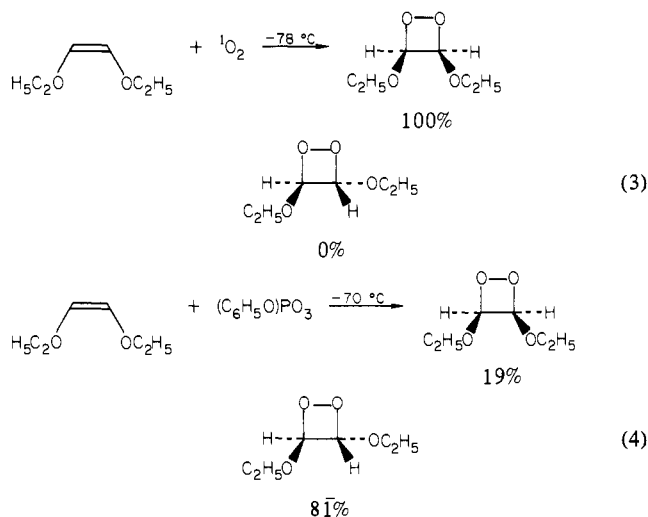
Isotope effect differences in the reactions of the isomeric tetramethylethylenes-*d*₆ have provided sensitive tests of mechanism in the singlet oxygen reaction⁴ and the reactions of azoophiles.⁵

(1) (a) Murray, R. W.; Kaplan, M. L. *J. Am. Chem. Soc.* 1968, 90, 537; 1968, 90, 4161; 1969, 91, 5358. (b) Wasserman, E.; Murray, R. W.; Kaplan, M. L.; Yager, W. A. *Ibid.* 1968, 90, 4160. (c) Koch, E. *Tetrahedron* 1970, 26, 3503.

(2) (a) Bartlett, P. D.; Mendenhall, G. D. *J. Am. Chem. Soc.* 1970, 92, 210. (b) Schaap, A. P.; Bartlett, P. D. *Ibid.* 1970, 92, 6055. (c) Bartlett, P. D.; Mendenhall, G. D.; Schaap, A. P. *Ann. N.Y. Acad. Sci.* 1970, 171, 79. (d) Bartlett, P. D.; Chu, H.-K. *J. Org. Chem.* 1980, 45, 3000.

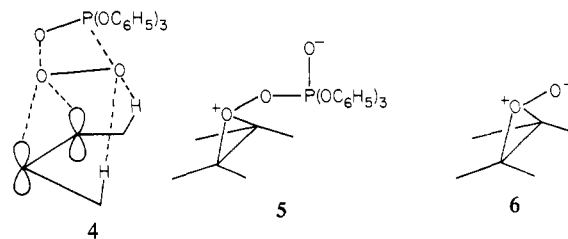
(3) Bartlett, P. D.; Schaap, A. P. *J. Am. Chem. Soc.* 1970, 92, 3223.

(4) (a) Grdina, M. B.; Orfanopoulos, M.; Stephenson, L. M. *J. Am. Chem. Soc.* 1979, 101, 3111. (b) Stephenson, L. M.; Grdina, M. J.; Orfanopoulos, M. *Acc. Chem. Res.* 1980, 13, 419.

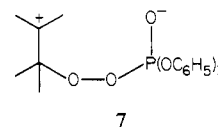


We have repeated these isotope effect mapping experiments with triphenyl phosphite ozonide (TPPO) and tetramethylethylenes-*d*₆. The results are presented in Table I.

In the case of the TPPO-mediated direct delivery of O₂, as in the free singlet oxygen case, also shown in Table I, it is obvious that only *cis* relationships of C-H and C-D bonds lead to an isotope competition. This previously led us to propose an olefin-bisecting approach⁴ of ¹O₂, a situation that must be very closely duplicated in the reaction of phosphite ozonides with olefins. An economical view of the TPPO-alkene reaction could be represented by transition state 4, the geometrically equivalent 5; or conceivably, the ozonide is sufficiently energetic to produce perepoxide 6.



As in singlet oxygen chemistry, the present experiments do not discriminate among geometrically equivalent pathways (4, 5, or 6 for example). A number of mechanisms can be eliminated, however, most prominently the zwitterionic pathway suggested by structure 7. As we have previously pointed out in arguments






concerning ¹O₂, such intermediates would predict equal *k_H/k_D* effects for olefins 2 and 3 (Table I), contrary to our findings. Since strong evidence supports zwitterions in phosphite ozonide-vinyl ether reactions^{2b} (see reaction 4), it is clear that a unified mechanism for ozonide-olefin reactions will be elusive. The situation is thus completely analogous to free singlet oxygen chemistry. Jefford and co-workers⁷ in particular have generated strong evidence for zwitterions in ¹O₂ reactions with unsymmetrical, electron-rich systems such as methoxynorbornene, while other evidence⁴ makes it highly unlikely that zwitterions (or di-

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(7) (a) Jefford, C. W. *Tetrahedron Lett.* 1979, 985. (b) Jefford, C. W.; Rimbault, C. G. *J. Am. Chem. Soc.* 1978, 100, 295. (c) Jefford, C. W.; Laffer, M. H.; Boschung, A. F. *J. Am. Chem. Soc.* 1972, 94, 8904. (d) Jefford, C. W.; Rimbault, C. G. *J. Org. Chem.* 1978, 43, 1908. (e) Jefford, C. W.; Boschung, A. F. *Helv. Chim. Acta* 1974, 57, 2242.

Table I. Isotope Effects in the Reaction of the Three Bis(trideuteriomethyl)dimethylethylenes with TPPO^a and ¹O₂^b

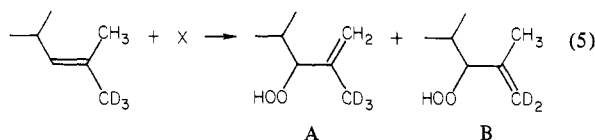
compd	olefin	k_H/k_D^a (TPPO)	k_H/k_D^b (¹ O ₂)
1		1.46	1.45
2		1.07	1.07
3		1.62	1.42

^a Reaction carried out at -70 °C (4 h), TPPO quenched with DABCO at -70 °C (1 h), and hydroperoxide product reduced with Ph₃P at -70 °C (1 h). ^b Reaction carried out at 0 °C by using rose bengal photosensitization.

radicals) are involved in ¹O₂ reactions with nonpolar alkenes.

While our isotope effect measurements require that the singlet oxygen reaction and the bimolecular reaction of TPPO with tetramethylethylene proceed through species of the same symmetry, our results do not demand common intermediates. The nonidentical k_H/k_D ratios for trans olefin (1.62, TPPO; 1.42 ¹O₂) are outside experimental error and suggest slight differences in reaction paths.

One would as well expect the regiochemical aspects of this reaction to vary with mode of oxygenation. In particular the now well-recognized propensity of free singlet oxygen to abstract H from the more crowded side of an olefin^{8,4b} might be expected to be somewhat attenuated, for steric reasons, in the TPPO case. Bartlett and Chu^{2d} have already identified small differences in product ratios with trimethylethylene and with 1,2-dimethylcyclohexene in the reaction of these olefins with TPPO and with ¹O₂. Even where the two sides of the olefin are sterically quite different as in eq 5, we can find only a small regiochemical effect.



X = ¹O₂, 86% A; 14% B
X = TPPO, 75% A; 25% B

In summary, these results provide yet another piece of evidence^{2,3} that direct low-temperature TPPO-olefin reactions do not proceed through free ¹O₂. Significantly, however, we have also demonstrated that the symmetry of the two reactions is the same and that the detailed characteristics of TPPO and ¹O₂ reactions with alkyl olefins differ only slightly. Very small differences in isotope and regiochemical effects can be found, suggesting to us that transfer of O₂ from TPPO is substantially accomplished in the transition state of the direct reaction and that the olefin reacts with an O₂ molecule almost completely free from steric and electronic influences by the phosphorus half of TPPO.

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Registry No. 1, 38132-23-9; 2, 38132-19-3; 3, 38132-24-0; A, 83026-80-6; B, 83026-81-7; (E)-2-(trideuteriomethyl)-4-methyl-2-pentene, 69432-96-8; rose bengal, 11121-48-5; TPPO, 29833-83-8; DABCO, 280-57-9; O₂, 7782-44-7; D₂, 7782-39-0.

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(9) Pryor, W. A.; Govindan, C. K. *J. Org. Chem.* **1981**, *46*, 4679. These authors have shown that direct TPPO-olefin reactions do not involve long-lived radical intermediates. Our results are clearly in accord with this view.

Diphosphenes (RP=PR). Synthesis and NMR Characterization

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There is growing interest in the topic of multiple bonding between the heavier main-group elements. Important recent developments include the isolation of stable compounds that feature double bonds between silicon atoms (disilenes)^{1,2} or phosphorus atoms (diphosphenes).³ In this communication we report (i) the synthesis of the first alkyl-substituted diphosphene, (ii) a new approach to the synthesis of diphosphenes, and (iii) NMR data pertinent to the phosphorus-phosphorus double bond.

In a typical experiment, 1,2-bis[tris(trimethylsilyl)methyl]diphosphene, (Me₃Si)₃CP=PC(SiMe₃)₃ (**1**) was prepared by dropwise addition of a solution of (Me₃Si)₃CPCl₂⁴ (6.20 g, 18.6 mmol) in THF (70 mL) to 42.0 mL of a 0.89 M solution of sodium naphthalene in THF at -78 °C. The solvent and naphthalene were removed by pumping in vacuo for several hours, leaving a red-brown residue. Separation of **1** from NaCl was achieved by treating the reaction mixture with hexane followed by filtration. Evaporation of the solvent left yellow, solid **1**, mp 152 °C (dec).⁵ Diphosphene **1** can also be prepared by treatment of (Me₃Si)₃CPCl₂ with a 4:1 mole ratio of (Me₃Si)₃CLi in Et₂O/THF solution. The 70-eV mass spectrum of **1** exhibits a parent peak at *m/e* 524 and peaks at *m/e* 509, 451, and 305, corresponding to fragmentation via loss of a methyl, one Me₃Si group, and three Me₃Si groups, respectively. A peak at *m/e* 293 corresponds to [(Me₃Si)₃CP₂]⁺. The high resolution mass spectrum for **1** showed the following: calcd, 524.2315; found, 524.2333. The ³¹P{¹H} NMR spectra at 36.43 MHz of **1** (CH₂Cl₂ solution) comprised only a singlet at +599.6 ppm.⁶ To the best of our knowledge, this is the largest ³¹P chemical shift measured thus far.⁷ Of great importance (vide infra) is the fact that the +599.6-ppm peak remains a singlet in proton-coupled ³¹P NMR experiments. Further proof of the formulation of **1** as a diphosphene stems from ¹H and ¹³C{¹H} NMR spectroscopy. All resonances are "deceptively simple" triplets due to coupling to two phosphorus nuclei.⁸ The splittings in the ¹H and ¹³C{¹H} spectra are *N*(PH) and *N*(PC) and correspond to [⁴*J*_{PH} + ⁵*J*_{PH}] and [⁶*J*_{PC} + ⁿ⁺¹*J*_{PC}] (*n* = 1, 3), respectively. NMR data are as follows: ¹H NMR (90 MHz) Me₃Si (t, δ 0.3, *N*(PH) = 0.8 Hz); ¹³C{¹H} NMR (20.0 MHz, Me₃Si) Si₃C (t, δ 33.2, *N*(PC) = 41.5 Hz), Me₃Si (t, δ 4.88, *N*(PC) = 4.91 Hz). The electronic spectrum of **1** (hexane) exhibits peaks at λ_{max} 349 and 477 nm.

Yoshifuji et al.³ have reported that the reaction of (2,4,6-tri-*tert*-butylphenyl)phosphorus dichloride (**2**, Chart I) with Mg in THF results in diphosphene **3**, a species for which they claim a ³¹P chemical shift of -59 ppm. In view of (i) the very positive chemical shift of the alkyl-substituted diphosphene **1** and (ii) the fact that compounds with P=C bonds generally exhibit ³¹P chemical shifts in the range +100 to +300 ppm,^{9,10} we were

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(2) Masamune, S.; Hanzawa, Y.; Murakami, S.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150-1152.

(3) Yoshifuji, M.; Shima, I.; Inamoto, N. *J. Am. Chem. Soc.* **1981**, *103*, 4587-4589.

(4) Issleib, K.; Schmidt, H.; Wirkner, C. Z. *Chem.* **1980**, *20*, 153.

(5) The conversion of (Me₃Si)₃CPCl₂ to **1** is virtually quantitative on the basis of ³¹P NMR spectroscopy. Isolated yields of **1** are ~80%.

(6) Positive ³¹P chemical shifts are downfield from external 85% H₃PO₄.

(7) The previous record was +513.2 ppm in the two-coordinate phosphorus cation [(Me₂N)(*t*-Bu)P]⁺. Cowley, A. H.; Lattman, M.; Wilburn, J. C. *Inorg. Chem.* **1981**, *20*, 2916-2919.

(8) A similar situation has been observed in the ¹H and ¹³C spectra of alkylated diphosphines. See: Ali, A. A. M.; Bocelli, G.; Harris, R. K.; Fild, M. J. *Chem. Soc., Dalton Trans.* **1980**, 638-344 and references therein.