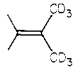
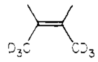
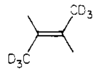
Table I. Isotope Effects in the Reaction of the Three Bis(trideuteriomethyl)dimethylethylenes with TPPO[a] and $^1O_2$ [b]

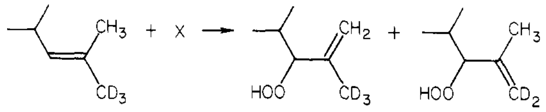
compd	olefin	k_H/k_D [a] (TPPO)	k_H/k_D [b] ($^1O_2$)
1		1.46	1.45
2		1.07	1.07
3		1.62	1.42

[a] Reaction carried out at −70 °C (4 h), TPPO quenched with DABCO at −70 °C (1 h), and hydroperoxide product reduced with Ph_3P at −70 °C (1 h). [b] Reaction carried out at 0 °C by using rose bengal photosensitization.

radicals) are involved in $^1O_2$ 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 $^1O_2$) 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 $^1O_2$. Even where the two sides of the olefin are sterically quite different as in eq 5, we can find only a small regiochemical effect.



(5)

A B

X = $^1O_2$, 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 $^1O_2$. Significantly, however, we have also demonstrated that the symmetry of the two reactions is the same and that the detailed characteristics of TPPO and $^1O_2$ reactions with alkyl olefins differ only slightly. Very small differences in isotope and regiochemical effects can be found, suggesting to us that transfer of O_2 *from* TPPO is substantially accomplished in the transition state of the direct reaction and that the olefin reacts with an O_2 molecule almost completely free from steric and electronic influences by the phosphorus half of TPPO.

Acknowledgment. This work was generously supported by the National Science Foundation through Grant No. CHE-80-12233.

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; O_2, 7782-44-7; D_2, 7782-39-0.

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[8] (a) Orfanopoulos, M.; Grdina, M. B.; Stephenson, L. M. *J. Am. Chem. Soc.* **1979**, *101*, 275. (b) Schulte-Elte, K. H.; Muller, B. L. Rautenstrauch, V. *Helv. Chim. Acta* **1978**, *61*, 2777.

[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, $(Me_3Si)_3CP{=}PC(SiMe_3)_3$ (**1**) was prepared by dropwise addition of a solution of $(Me_3Si)_3CPCl_2$[4] (6.20 g, 18.6 mmol) in THF (70 mL) to 42.0 mL of a 0.89 M solution of sodium napthelenide in THF at −78 °C. The solvent and napthalene 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 $(Me_3Si)_3CPCl_2$ with a 4:1 mole ratio ratio of $(Me_3Si)_3CLi$ in Et_2O/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 Me_3Si group, and three Me_3Si groups, respectively. A peak at *m/e* 293 corresponds to $[(Me_3Si)_3CP_2]^+$. The high resolution mass spectrum for **1** showed the following: calcd, 524.2315; found, 524.2333. The $^{31}P\{^1H\}$ NMR spectra at 36.43 MHz of **1** (CH_2Cl_2 solution) comprised only a singlet at +599.6 ppm.[6] To the best of our knowledge, this is the largest ^{31}P 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 ^{31}P NMR experiments. Further proof of the formulation of **1** as a diphosphene stems from ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. All resonances are "deceptively simple" triplets due to coupling to two phosphorus nuclei.[8] The splittings in the ^1H and $^{13}C\{^1H\}$ spectra are N(PH) and N(PC) and correspond to $|^4J_{PH} + {}^5J_{PH}|$ and $|^nJ_{PC} + {}^{n+1}J_{PC}|$ (n = 1, 3), respectively. NMR data are as follows: ^1H NMR (90 MHz) Me_3Si (t, δ 0.3, N(PH) = 0.8 Hz); $^{13}C\{^1H\}$ NMR (20.0 MHz, Me_4Si) Si_3C (t, δ 33.2, N(PC) = 41.5 Hz), Me_3Si (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 ^{31}P 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 ^{31}P chemical shifts in the range +100 to +300 ppm,[9,10] we were

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[1] West, R.; Fink, M. J.; Michl, J. *Science (Washington, D.C.)* **1981**, *214*, 1343–1344.

[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 $(Me_3Si)_3CPCl_2$ to **1** is virtually quantiative on the basis of ^{31}P NMR spectroscopy. Isolated yields of **1** are ~80%.

[6] Positive ^{31}P chemical shifts are downfield from external 85% H_3PO_4.

[7] The previous record was +513.2 ppm in the two-coordinate phosphorus cation $[(Me_2N)(t\text{-}Bu)P]^+$. 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 ^{13}C 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.

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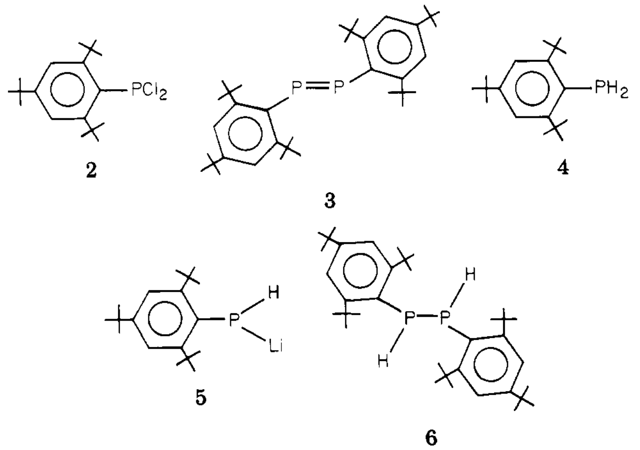
Chart I



prompted to reinvestigate the reaction of **2** with Mg in THF. We find that this is not a straightforward reaction. $^{31}P\{^1H\}$ peaks are detectable at +494 and −64 ppm. In proton-coupled experiments the +494-ppm peak remained a singlet, while the one at −64 ppm became a six-line AA′XX′ pattern. The −64-ppm peak, therefore, cannot correspond to the P=P bonded compound, **3**. Confirmation that the ^{31}P chemical shift of **3** is, in fact, +494 ppm was provided by dissolving crystals with properties identical with those of **3** in CH_2Cl_2 and recording both $^{31}P\{^1H\}$ and ^{31}P NMR spectra.

We turn next to the identity of the material responsible for the −64-ppm peak (−59 ppm as reported by Yoshifuji et al.[3]). Reduction of **2** with $LiAlH_4$ in Et_2O solution affords high yields of the primary phosphine **4**, mp 144 °C. NMR data for **4** are as follows: ^{31}P NMR (36.43 MHz) δ −132 (t, J_{PH} = 209 Hz); ^1H NMR (90 MHz) *p-t*-Bu (s, 9 H, δ 1.32), *o-t*-Bu (s, 18 H, δ 1.60), P–H (d, 2 H, δ 4.22 J_{PH} = 209 Hz), C–H (d, 2 H, δ 7.52, J_{PCCCH} = 2.3 Hz). Treatment of **4** with *n*-BuLi results in the monolithio species[11,12] **5**, which is responsible for a solvent-dependent doublet in ^{31}P NMR spectra: THF (d, δ −110, J_{PH} = 171.8 Hz), Et_2O (d, δ −125, J_{PH} = 189.0 Hz). The reaction of **5** with CCl_4 affords 1,2-bis(2,4,6-tri-*tert*-butylphenyl)diphosphine (**6**) in virtually quantitative yield.[13] The ^{31}P and $^{31}P\{^1H\}$ NMR spectra of **6** are identical with those recorded for reaction mixtures of **2** and Mg in THF. ^1H NMR data (90 MHz) for **6** are as follows: *p-t*-Bu (s, 18 H, δ 1.3), *o-t*-Bu (s, 36 H, δ 1.4), P–H (AA′XX′ pattern, 2 H, δ 4.7, J_{PH} = 221.0, J_{PP} = 192.4, J_{PPH} = 16.0, J_{HPPH} = 1.0 Hz). In summary, the reaction of **2** with Mg in THF results inter alia in **3** and **6**. The ^{31}P chemical shift of the diphosphene **3** should be +494 ppm and not −59 ppm as reported by Yoshifuji et al.[3] The compound responsible for the −59-ppm ^{31}P NMR peak is, in fact, the diphosphine **6**, which can be regarded as the product of oxidative addition of H_2 to the P=P bond.

The reactivity of **1**[14] and theoretical aspects[15] of the phosphorus–phosphorus double bond are under active investigation.

Acknowledgment. Generous financial support from the National Science Foundation (Grant CHE-8205871) and the Robert A. Welch Foundation is gratefully acknowledged.

Registry No. 1, 83115-11-1; **2**, 79074-00-3; **3**, 79073-99-7; **4**, 83115-12-2; **5**, 83115-13-3; **6**, 83115-14-4; $(Me_3Si)_3CPCl_2$, 75235-85-7; $(Me_4Si)_3CLi$, 28830-22-0; sodium naphthelenide, 3481-12-7.

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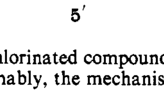
(9) For a summary of ^{31}P NMR data on phosphaalkenes, see: Appel, R.; Knoll, F.; Ruppert, I. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 731–744 and references therein.

(10) The only phosphaalkene with a negative ^{31}P chemical shift is HP=CF_2.[9]

(11) Compound **4** undergoes monolithiation even if excess *n*-BuLi, *n*-BuLi/TMEDA, MeLi (−60 °C), or KH is employed. Presumably this is due to the steric bulk of the 2,4,6-tri-*tert*-butylphenyl group. Interestingly, however, the sterically congested phosphine[4] $(Me_3Si)_3CPH_2$ will undergo dilithiation with *n*-BuLi.

(12) Further proof that **4** undergoes only monolithiation was provided by D_2O quenching of **5**, which results in **5′**: ^{31}P NMR (Et_2O) (d of t, δ −133, J_{PH} = 189.0, J_{PD} = 32.2 Hz).



5′

(13) A variety of other chlorinated compounds will convert **5** to **6**, e.g., **2**, *t*-$BuPCl_2$, and PCl_3. Presumably, the mechanism involves lithium–chlorine exchange.

(14) Preliminary NMR studies reveal that **1** exhibits short-term stability with respect to water and oxygen. Solutions of **1** in organic solvents degrade over a number of hours as evidence by the appearance of new ^{31}P NMR peaks between +20 and +40 ppm.

(15) The model diphosphene HP=PH has been investigated by ab initio molecular orbital calculations. Boggs, J. E.; Cowley, A. H.; Lee, J.-G., to be submitted for publication.

Cis Selectivity of "Salt-Free" Wittig Reactions: A "Leeward Approach" of the Aldehyde at the Origin?

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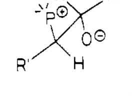
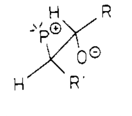
Received April 28, 1982

Despite its great practical importance, the cis selectivity[1] encountered in Wittig olefin syntheses with "salt-free" triphenylphosphonio ylides and aldehydes has not yet found a conclusive explanation. The conformational analysis presented in this communication provides a new and successful approach to solve this question.

First efforts[2] of rationalization invoked an anti-periplanar alignment of the combining PC and CO dipoles. The threo intermediate (**1B**) should then suffer from the gauche interaction

1A





1B

of two organic groups (R = alkyl or aryl, R′ = alkyl) and consequently the erythro stereoisomer (**1A**) would be produced preferentially. But not only did the basic assumption, the anti-periplanar orientation, remain unsubstantiated, also the magnitude of cis selectivity could hardly be understood on the basis of such conformational effects.[3]

The next attempts[4] to deal with the problem postulated an unprecedented geometry of the adduct-generating transition state. The aldehyde was thought to approach the ylide in a plane perpendicular to that occupied by the ylide center to minimize steric repulsions. The formyl hydrogen would, of course, point toward the ylide (**2A**). In the moment of carbon–carbon linking, it would turn away from the bulky alkyl group R′, thus imposing a cis relationship on the groups R and R′. The concept of the perpendicular approach became popular when oxaphosphetanes were recognized to be generally the only metastable intermediates in Wittig reactions.[5] This orientation (transition state **2B** or **2C**)

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(1) (a) Schlosser, M.; Christmann, K. F. *Justus Liebigs Ann. Chem.* **1967**, *708*, 1. (b) Schlosser, M. *Top. Stereochem.* **1970**, *5*, 1.

(2) (a) Bergelson, L. D.; Shemyakin, M. M. *Angew. Chem.* **1964**, *76*, 113; *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 250. (b) Rüchardt, C.; Panse, P.; Eichler, S. *Chem. Ber.* **1967**, *100*, 1144.

(3) Reference 1a, pp 17–18.

(4) (a) Schneider, W. P. *Chem. Commun.* **1969**, 785. (b) Schlosser, M.; Heinz, G. *Angew. Chem.* **1968**, *80*, 849; *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 820.

(5) (a) Vedejs, E.; Snoble, K. A. J. *J. Am. Chem. Soc.* **1973**, *95*, 5778. (b) Vedejs, E.; Meier, G. P.; Snoble, K. A. J. *Ibid.* **1981**, *103*, 2823. (c) As specified in ref 5b, these authors, however, favor a tilted over a plane-parallel transition state mainly for stereochemical (i.e., geometrical) rather than for orbital symmetry reasons.

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