

of 4-6 kcal/mol in this class of compounds.

Acknowledgment. We thank Professor E. Ōsawa for helpful comments and suggestions regarding this manuscript. The EC-Japan Center for Industrial Research, Fundación Ramón Areces, and DGICYT (project no.

PB86-0320) are gratefully acknowledged for financial support.

Registry No. 1, 92-52-4; 2, 776-35-2; 3, 1015-80-1; 4, 1082-12-8; 5, 366-18-7; 6, 97919-82-9; 7, 97919-83-0; 8, 97919-84-1; 9, 125568-48-1; 10, 125568-49-2.

Nucleophilic Addition of Phosphines to Carbonyl Groups. Isolation of 1-Hydroxy Phosphonium and 1-(Trimethylsiloxy) Phosphonium Salts and the Crystal Structure of (1-Hydroxy-1-methylethyl)triethylphosphonium Bromide

Soon W. Lee and William C. Trogler*

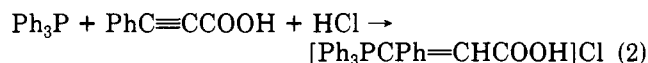
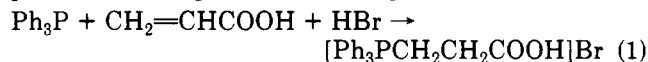
Department of Chemistry, D-006, University of California at San Diego, La Jolla, California 92093-0506

Received January 9, 1990

1-Hydroxy phosphonium salts and 1-(trimethylsiloxy) phosphonium salts can be isolated by nucleophilic addition of a small basic phosphine (PMe₃ or PEt₃) to the carbonyl carbon of aldehydes or ketones in the presence of Br₂-acetone (a source of anhydrous HBr), anhydrous acids, or chlorotrimethylsilane as trapping agents. The crystal structure of [(CH₃)₂C(OH)(PEt₃)]Br, Ib, was determined through X-ray diffraction. Ib crystallizes in the monoclinic system, space group P2₁/n with lattice constants *a* = 7.304 (3) Å, *b* = 12.004 (4) Å, *c* = 14.164 (5) Å, β = 93.33 (3)°, and *Z* = 4. Least-squares refinement of the structure led to a *R* (*R*_w) factor of 0.042 (0.043) for 732 unique reflections of *I* > 3σ(*I*) and for 62 least-squares variables. The phosphorous atom and all carbon atoms adopt sp³ hybridization. The C-O bond distance of 1.429 (10) Å indicates a normal C-O single bond; however, the P-C bond to the carbonyl derived carbon (1.877 (10) Å) is significantly longer than the other P-C bonds (1.80 (1) Å av).

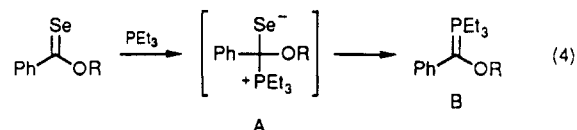
Introduction

Phosphonium salts are usually prepared from the reaction between phosphines and alkyl halides, and these salts are readily transformed to phosphorus ylides by treatment with base.¹ (2-Hydroxyalkyl)phosphonium salts are an important class of compounds because of their use in the mechanistic investigation of the Wittig reaction and their versatile synthetic utility.¹ Recently a general synthesis of (2-hydroxyalkyl)-, (3-hydroxyalkyl)-, and (4-hydroxyalkyl)phosphonium salts was reported from the reaction between triphenylphosphine and cyclic ethers in the presence of strong acids.² Tertiary phosphines are also known to attack at unsaturated carbon atoms and add smoothly to unsaturated aldehydes and esters in the presence of strong mineral acids (eqs 1, 2, and 3).³ Hansen

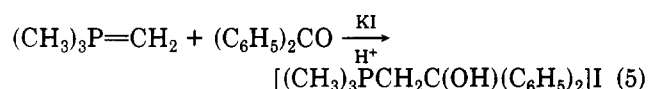


reported the reaction between *O*-alkyl selenoesters and PEt₃, which includes an intermediate A from nucleophilic attack of the phosphine on a selenoyl carbon;⁴ however,

this intermediate was not isolated (eq 4). Wittig and



Rieber reacted solutions of trimethylphosphonium methylide with benzophenone and isolated a low yield of impure (2,2-diphenyl-2-hydroxyethyl)trimethylphosphonium iodide after quenching with acid and potassium iodide.⁵



It has also been difficult to obtain structural data for tetrahedral intermediates formed by nucleophilic addition to a carbonyl carbon.^{1a,7} Weak amine-carbonyl interac-

(4) Hansen, P.-E. *J. Chem. Soc., Perkin Trans. 1* 1979, 1627.

(5) Wittig, G.; Rieber, M. *Justus Liebigs Ann. Chem.* 1949, 562, 177. Trialkyl ylids show enhanced reactivity over aryl analogues.⁶

(6) Johnson, A. W.; LaCount, R. B. *Tetrahedron* 1960, 9, 130.

(7) (a) Asubiojo, O. I.; Blair, L. K.; Brauman, J. I. *J. Am. Chem. Soc.* 1975, 97, 6685. (b) Rogers, G. A.; Bruce, T. C. *Ibid.* 1974, 96, 2481. (c) Khouri, F.; Kaloustian, M. K. *Ibid.* 1979, 101, 2249. (d) O'Leary, M. H.; Marlier, J. F. *Ibid.* 1979, 101, 3300. (e) Tee, O. S.; Trani, M.; McClelland, R. A.; Seaman, N. E. *Ibid.* 1982, 104, 7219. (f) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 290. (g) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Harper and Row: New York, 1981. (h) McClelland, R. A.; Santry, L. J. *Acc. Chem. Res.* 1983, 16, 394. (i) Capon, B.; Ghosh, A. K.; Grieve, D. M. A. *Acc. Chem. Res.* 1981, 14, 306. (j) Bender, M. L. *Chem. Rev.* 1960, 60, 53. (k) Jencks, W. P. *Catalysis in Chemistry and Enzymology*; McGraw-Hill: New York, 1968. (l) Bruce, T. C.; Benkovic, S. *Bioorganic Mechanisms*; W. A. Benjamin: New York, 1966; Vol. 1. (m) Jencks, W. P. *Chem. Rev.* 1972, 72, 705. References in the above.

(1) (a) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley and Sons: New York, 1985; p 846. (b) Vedejs, E.; Meier, G. P.; Snoble, K. A. *J. Am. Chem. Soc.* 1981, 103, 2823. (c) C-Rouhou, F.; Bigot, Y. L.; Gharbi, Y. L.; Delmas, M.; Gaset, A. *Synth. Commun.* 1986, 1739. (d) Johnson, A. W. *Ylid Chemistry*; Academic Press: New York, 1966. (e) Maercker, A. *Org. React.* 1965, 14, 270.

(2) Yamamoto, S.; Okuma, K.; Ohta, H. *Bull. Chem. Soc. Jpn.* 1988, 61, 4476.

(3) Corbridge, D. E. C. *Phosphorus*; Elsevier: Amsterdam, 1985; p 209.

Table I. Spectroscopic and Analytical Data for 1-Hydroxy and 1-(Trimethylsiloxy) Phosphonium Salts Prepared

compound	yield, %	$\nu_{\text{OH}},^a \text{ cm}^{-1}$	mp, °C	anal. (%) calcd (obsd)	$^1\text{H NMR (CDCl}_3), \delta$
Ia, $[(\text{CH}_3)_2\text{C}(\text{OH})\text{PMe}_3]\text{Br}$	80	3262	99–101	C, 33.51 (33.67); H, 7.50 (7.00)	1.35 (dd, $\text{CH}_3, J_{\text{H-H}} = 7 \text{ Hz}, J_{\text{P-H}} = 18 \text{ Hz}$), 1.83 (d, $\text{PCH}_3, J_{\text{P-H}} = 15 \text{ Hz}$), 4.59 (q, $\text{CH}, J_{\text{H-H}} = 7 \text{ Hz}$)
Ib, $[(\text{CH}_3)_2\text{C}(\text{OH})\text{PEt}_3]\text{Br}$	55	3148	<i>b</i>	C, 42.04 (41.52); H, 8.62 (8.94)	1.32 (dt, $\text{PCH}_2\text{CH}_3, J_{\text{H-H}} = 7 \text{ Hz}, J_{\text{P-H}} = 17 \text{ Hz}$), 1.68 (d, $\text{CH}_3, J_{\text{P-H}} = 15 \text{ Hz}$), 2.38 (dq, $\text{PCH}_2, J_{\text{H-H}} = 7 \text{ Hz}, J_{\text{P-H}} = 15 \text{ Hz}$), 6.29 (d, $\text{CH}, J_{\text{P-H}} = 8 \text{ Hz}$)
IIa, $[(\text{CH}_3)_2\text{C}(\text{OH})\text{PMe}_3]\text{Cl}$	85	3258	163–166	C, 42.24 (41.78); H, 9.45 (9.37)	1.62 (d, $\text{CH}_3, J_{\text{P-H}} = 16 \text{ Hz}$), 2.10 (d, $\text{PCH}_3, J_{\text{P-H}} = 14 \text{ Hz}$)
IIb, $[(\text{CH}_3)_2\text{C}(\text{OH})\text{PEt}_3]\text{Cl}$	91	3158	<i>b</i>	C, 50.82 (50.80); H, 10.43 (10.40)	1.31 (dt, $\text{PCH}_2\text{CH}_3, J_{\text{H-H}} = 8 \text{ Hz}, J_{\text{P-H}} = 19 \text{ Hz}$), 1.65 (d, $\text{CH}_3, J_{\text{P-H}} = 15 \text{ Hz}$), 2.48 (m, PCH_2)
IIIa, $[(\text{CH}_3)_2\text{C}(\text{OH})\text{PMe}_3][p\text{-MeC}_6\text{H}_4\text{SO}_3]$	99	3200	131–133	C, 50.97 (50.52); H, 7.57 (7.54)	1.40 (d, $\text{CH}_3, J_{\text{P-H}} = 13 \text{ Hz}$), ^c 1.88 (d, $\text{PCH}_3, J_{\text{P-H}} = 14 \text{ Hz}$), 2.29 (s, CH_3), 7.08–7.60 (m, 4 H, C_6H_5)
IIIb, $[(\text{CH}_3)_2\text{C}(\text{OH})\text{PEt}_3][p\text{-MeC}_6\text{H}_4\text{SO}_3]$	99	3158	<i>b</i>	C, 55.15 (54.74); H, 8.39 (8.39)	1.27 (dt, $\text{PCH}_2\text{CH}_3, J_{\text{H-H}} = 8 \text{ Hz}, J_{\text{P-H}} = 17 \text{ Hz}$), 2.18 (s, CH_3), 2.23 (m, PCH_2), 7.20–7.80 (m, 4 H, C_6H_5)
IVa, $[\text{PhCH}(\text{OTMS})\text{PMe}_3]\text{Cl}$	89	–	151–153	C, 53.69 (52.85); H, 8.32 (8.20)	0.25 (s, 9 H, TMS), 2.11 (d, 9 H, $\text{PCH}_3, J_{\text{P-H}} = 15 \text{ Hz}$), 6.89 (d, $\text{CH}, J_{\text{P-H}} = 8 \text{ Hz}$), 7.35–7.8 (m, 5 H)
IVb, $[\text{PhCH}(\text{OTMS})\text{PEt}_3]\text{Cl}$	48	–	110–112	C, 57.72 (58.14); H, 9.08 (8.88)	0.24 (s, 9 H, TMS), 1.12–1.47 (dt, $\text{PCH}_2\text{CH}_3, J_{\text{H-H}} = 9 \text{ Hz}, J_{\text{P-H}} = 18 \text{ Hz}, \text{CH}_3$), 2.56 (dq, $\text{PCH}_2, J_{\text{H-H}} = 9 \text{ Hz}, J_{\text{P-H}} = 8 \text{ Hz}$), 7.03 (d, $\text{CH}, J_{\text{P-H}} = 8 \text{ Hz}$), 7.3–7.7 (m, 5 H)
Va, $[(\text{CH}_3)\text{CH}(\text{OH})\text{PMe}_3]\text{Cl}$	69	3183	209–211	C, 38.35 (37.45); H, 9.01 (9.38)	1.48 (dd, $\text{CH}_3, J_{\text{H-H}} = 8 \text{ Hz}, J_{\text{P-H}} = 16 \text{ Hz}$), 1.95 (d, $\text{PCH}_3, J_{\text{P-H}} = 15 \text{ Hz}$), δ 4.93 (q, $\text{CH}, J_{\text{H-H}} = 8 \text{ Hz}$)
Vb, $[(\text{CH}_3)\text{CH}(\text{OH})\text{PEt}_3]\text{Cl}$	68	3173	193–195	C, 48.36 (47.17); H, 10.15 (10.58)	1.27–1.96 (m, 12 H, CH_3 and PCH_2CH_3), 2.57 (dq, $\text{PCH}_2, J_{\text{H-H}} = 8 \text{ Hz}, J_{\text{P-H}} = 15 \text{ Hz}$), 5.95 (q, $\text{CH}, J_{\text{H-H}} = 7.5 \text{ Hz}$)

^a KBr pellet. ^b Too hygroscopic to be measured accurately. ^c DMSO-*d*₆.

tions in several crystal structures have permitted the construction of a likely reaction coordinate for nucleophilic addition to a carbonyl.⁸ Addition of PR_3 (R = Me, Et, OMe) to $\text{Cp}^*\text{Cl}_3\text{TaSiMe}_3$ under a CO atmosphere yields $\text{Cp}^*\text{Cl}_3\text{Ta}[\eta^2\text{-OC}(\text{PR}_3)\text{SiMe}_3]$, which has been characterized crystallographically for R = Et.⁹ Addition of PMe_3 to the η^2 -acyl complex $\text{Cp}(\text{NO})\text{IMo}[\eta^2\text{-OC}(p\text{-C}_6\text{H}_4\text{Me})]$ yields¹⁰ $\text{Cp}(\text{NO})\text{IMo}[\eta^2\text{-OC}(\text{PMe}_3)(p\text{-C}_6\text{H}_4\text{Me})]$. The reaction between Co^{2+} , PEt_3 , and $\text{CH}_3\text{C}(\text{CH}_2\text{PPh}_2)_3$ yields $[\text{Et}_3\text{P}(\text{CH}_3)_2\text{OH}]\text{BPh}_4$ as a side product in acetone solvent,¹¹ and $[\text{Ph}_3\text{P}(\text{CH}_2\text{OH})]\text{BF}_4$ has been produced from the reaction between paraformaldehyde and PPh_3 in $\text{Et}_2\text{O-HBF}_4$.¹² Compounds of the formula $[\text{RC}(\text{O})\text{-OCR}'\text{HPR}_3]\text{X}$ form on addition of PR_3 to a 1:1 acyl halide-aldehyde mixture.¹³ In one report¹⁴ the addition of

HBF_4 to a benzaldehyde- PPh_3 mixture precipitated a solid formulated as $[\text{PhHC}(\text{OH})\text{PPh}_3]\text{BF}_4$. Herein we describe the direct preparation of 1-hydroxy phosphonium salts and 1-(trimethylsiloxy) phosphonium salts from nucleophilic addition of a small basic phosphine (PMe_3 or PEt_3) to the carbonyl carbon of ketones or aldehydes in the presence of electrophilic trapping agents such as Br_2 -acetone, anhydrous acids, or TMSCl . We also report the molecular structure of one of these adducts.

Experimental Section

Reactions were performed with standard Schlenk and cannula filtration techniques under a nitrogen atmosphere. Glassware was either oven-dried or flame-dried before use. Diethyl ether and tetrahydrofuran solvents were refluxed over sodium or potassium benzophenone ketyl and distilled under nitrogen or by vacuum transfer. Dichloromethane and acetone were distilled over CaH_2 and K_2CO_3 , respectively. Trimethylsilyl chloride was distilled and stored under N_2 . The Br_2 and 4 M HCl /dioxane were freeze-pump-thaw-degassed before use and stored under nitrogen. Toluenesulfonic acid was vacuum dried for 12 h at 80 °C. Trimethylphosphine and triethylphosphine were purchased from commercial sources and used without purification.

(8) (a) Bürgi, H. B.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065. (b) Dunitz, J. D. *X-ray Analysis and the Structure of Small Molecules*; Cornell University Press: Ithaca, 1979.

(9) Arnold, J.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J.; Arif, A. M. *J. Am. Chem. Soc.* **1989**, *111*, 149.

(10) Bonnesen, P. V.; Yau, P. K. L.; Hersh, W. H. *Organometallics* **1987**, *6*, 1587.

(11) Bianchini, C.; Masi, C.; Mealli, C.; Meli, A.; Sabat, M. *Gazz. Chim. Ital.* **1986**, *116*, 201.

(12) Wittig, G.; Schlosser, M. *Chem. Ber.* **1961**, *94*, 1373.

(13) Anders, E.; Gassner, T. *Chem. Ber.* **1984**, *117*, 1034.

(14) Anders, E.; Gassner, T.; Stankowiak, A. *Chem. Ber.* **1985**, *118*, 124.

¹H NMR spectra were obtained with either a Varian EM-390 or a General Electric-QE 300 MHz spectrometer, and the latter instrument was used to measure ¹³C NMR spectra. IR spectra were recorded with an IBM IR/32 spectrometer. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory. Spectroscopic and analytical data for all new compounds are collected in Table I.

Synthesis of [(CH₃)₂C(OH)PMe₃]Br, Ia. After addition of 15 mL of acetone containing 20 drops of Br₂ to 0.5 mL of PMe₃ (4.92 mmol) in 10 mL of acetone cooled to -78 °C in a 2-propanol/dry ice bath, a white solid began to appear in the solution. After 5 min the cold bath was removed, and the solution was allowed to stand for 4 h. The white crystals that formed were collected by filtration and washed with ether (3 × 15 mL) to yield 0.85 g (80%) of Ia.

Synthesis of [(CH₃)₂C(OH)PET₃]Br, Ib. After addition of 5 mL of acetone containing 20 drops of Br₂ to 1 mL of triethylphosphine (6.8 mmol) in 10 mL of acetone at -78 °C, a white solid began to appear in the solution. After 5 min the cold bath was removed, and the solution was allowed to stand for 1 day. The solvent was decanted, and the remaining white crystals were washed with Et₂O (20 mL × 3) and dried under vacuum to yield 0.95 g (54%) of Ib. Crystals of Ib are hygroscopic.

Synthesis of [(CH₃)₂C(OH)PMe₃]Cl, IIa. After addition of 2.5 mL of 4 M HCl/dioxane in 10 mL of acetone to 1 mL of PMe₃ (9.83 mmol) in 20 mL of acetone at -78 °C, a white solid formed immediately. The mixture was allowed to stand for 8 h, and 30 mL of Et₂O was added to form white crystals. The crystals were washed with Et₂O and dried under vacuum to yield 1.42 g (85%) of IIa.

Synthesis of [(CH₃)₂C(OH)PET₃]Cl, IIb. On addition of 2 mL of 4 M HCl/dioxane in 20 mL of acetone to 1 mL of PET₃ (6.8 mmol) in 10 mL of acetone at -78 °C, a white solid appeared in the solution. After 5 min the cold bath was removed, and the solution was allowed to warm slowly to room temperature to yield a clear solution after 16 h. Addition of 30 mL of Et₂O to this solution formed white hygroscopic crystals that were collected by filtration and washed with Et₂O to yield 1.32 g (91%) of IIb.

Synthesis of [(CH₃)₂C(OH)PMe₃][p-SO₃C₆H₄CH₃], IIIa. Addition of 2.0 g (10.5 mmol) of *p*-toluenesulfonic acid in 20 mL of acetone to 1 mL of PMe₃ (9.83 mmol) dissolved in 10 mL of acetone at -78 °C produced a white powder. The solution was allowed to warm to room temperature, and after 16 h the solvent was decanted; the white crystals were washed with Et₂O (15 mL × 3) and dried under vacuum to yield 3.0 g (99%) of IIIa.

Synthesis of [(CH₃)₂C(OH)PET₃][p-SO₃C₆H₄CH₃], IIIb. On addition of 1.5 g (7.89 mmol) of *p*-toluenesulfonic acid dissolved in 20 mL of acetone to 1 mL of PET₃ (6.8 mmol) dissolved in 10 mL of acetone at -78 °C, a white powder appeared in the solution. After 4 h and warming to room temperature the solvent was decanted; the crystals were washed with Et₂O (15 mL × 3) and dried under vacuum to yield 2.3 g (99%) of white hygroscopic IIIb.

Synthesis of [(C₆H₅)CH(OTMS)(PMe₃)]Cl, IVa. On addition of 1.3 mL (10.2 mmol) of TMSCl (chlorotrimethylsilane) in 20 mL of THF to a mixture of 1 mL (9.83 mmol) of benzaldehyde and 1 mL (9.83 mmol) of PMe₃ in 40 mL of THF at -78 °C, a white powder appeared in the solution. After 5 min the solution was allowed to warm gradually to room temperature. After 12 h the solution was filtered, washed with Et₂O, and dried under vacuum to yield white crystals 3.05 g (89%) of IVa.

Synthesis of [(C₆H₅)CH(OTMS)(PET₃)]Cl, IVb. A solution of 1.8 mL (14.2 mmol) of TMSCl in 20 mL of THF was layered on 40 mL of THF solution containing 2 mL (13.6 mmol) of PET₃ and 1.4 mL (13.8 mmol) of benzaldehyde at -78 °C. White powder formed immediately. The solution was allowed to warm to room temperature over 12 h, and the solvent was removed to yield a gellike product. Then 60 mL of Et₂O was added to yield a white suspension, which was filtered and dried under vacuum to obtain 2.17 g of IVb as a white powder (48%).

Synthesis of [(CH₃)CH(OH)PMe₃]Cl, Va. On addition of 5 mL of PMe₃ (19.6 mmol) to 1 mL of CH₃CHO (17.9 mmol) in 30 mL of THF at -78 °C, a white powder appeared in the solution. After 5 min the cold bath was removed and the solution was allowed to stand for 12 h. The solvent was decanted; the white crystals were washed with Et₂O (20 mL × 3) and dried under

Table II. Crystallographic Data for [(CH₃)₂C(OH)(PET₃)]Br

chemical formula: C ₉ H ₂₃ OPBr	fw: 258.16
space group: P2 ₁ /n	T: 23 °C
a = 7.304 (3) Å	λ = 0.71073 Å
b = 12.004 (4) Å	μ = 33.7 cm ⁻¹
c = 14.165 (5) Å	2θ range: 3–40°
β = 93.33 (3) Å	R = 0.042
V = 1240 (1) Å ³	R _w = 0.043
largest residual peak, e/Å ³ : 0.31	Z = 4
no. unique data: 1126	scan type: θ–2θ
no refl used (I > 3σ(I)): 732	no. parameters: 62

Table III. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å² × 10³) for Ib

	x	y	z	U (eq) ^a
Br	2291 (2)	2817 (1)	1098 (1)	52 (1)
P(1)	3612 (5)	4748 (2)	7487 (1)	30 (1)
C(11)	5585 (15)	4151 (7)	8127 (5)	48 (3)
C(12)	5237 (16)	3124 (6)	8718 (5)	48 (3)
C(13)	2756 (15)	3763 (6)	6603 (5)	38 (2)
C(14)	1326 (17)	4258 (7)	5896 (5)	55 (3)
C(15)	4354 (16)	5991 (6)	6929 (5)	45 (2)
C(16)	5919 (18)	5803 (7)	6260 (6)	70 (3)
C(21)	1761 (15)	5145 (6)	8289 (5)	36 (2)
C(22)	607 (16)	4167 (7)	8529 (5)	53 (3)
C(23)	2659 (15)	5719 (6)	9172 (5)	41 (2)
O(1)	738 (12)	5934 (4)	7716 (4)	47 (2)

^a Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Bond Distances (Å) and Bond Angles (deg) for Ib

P(1)–C(11)	1.805 (10)	P(1)–C(13)	1.808 (8)
P(1)–C(15)	1.787 (8)	P(1)–C(21)	1.877 (10)
C(11)–C(12)	1.520 (11)	C(13)–C(14)	1.525 (13)
C(15)–C(16)	1.543 (15)	C(21)–C(22)	1.496 (13)
C(21)–C(23)	1.541 (11)	C(21)–O(1)	1.429 (10)
C(11)–P(1)–C(13)	108.8 (4)	C(11)–P(1)–C(15)	107.4 (5)
C(13)–P(1)–C(15)	109.9 (3)	C(11)–P(1)–C(21)	112.3 (4)
C(13)–P(1)–C(21)	110.7 (5)	C(15)–P(1)–C(21)	107.6 (4)
P(1)–C(11)–C(12)	116.4 (8)	P(1)–C(13)–C(14)	113.4 (5)
P(1)–C(15)–C(16)	113.8 (6)	P(1)–C(21)–C(22)	111.9 (6)
P(1)–C(21)–C(23)	108.5 (7)	C(22)–C(21)–C(23)	112.7 (6)
P(1)–C(21)–O(1)	101.3 (5)	C(22)–C(21)–O(1)	111.5 (8)
C(23)–C(21)–O(1)	110.4 (6)		

vacuum to yield 1.93 g (69%) of hygroscopic Va.

Synthesis of [(CH₃)CH(OH)PET₃]Cl, Vb. On addition of 5 mL of 4 M HCl/dioxane in 15 mL of THF to a mixture of 3 mL of PET₃ (20.4 mmol) and 1 mL of CH₃CHO (17.9 mmol) in 30 mL of THF at -78 °C, a white powder formed immediately. After 5 min the cold bath was removed and the solution was allowed to stand for 6 h. The solvent was decanted; the white powder was washed with Et₂O (20 mL × 3) and dried under vacuum to yield 2.41 g (68%) of hygroscopic Vb.

X-ray Structure Determination of Ib. X-ray data were collected with use of a Nicolet R3m/V diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. Crystal and intensity data are given in Table II. The orientation matrix and unit cell parameters were determined from 20 machine centered reflections with 15° < 2θ < 30°. Intensities of three check reflections were monitored after every 100 reflections during data collection. Intensities were corrected for Lorentz and polarization effects. No absorption correction was applied. All calculations were carried out on a Microvax II computer with use of the SHELXTL PLUS program package.

A white crystal of Ib, shaped as a block, of approximate dimensions 0.2 × 0.3 × 0.4 mm, was mounted on a glass fiber for crystal and intensity data collection. The unit cell parameters and systematic absences, *h*0*l* (*h* + *l* = 2*n* + 1) and 0*k*0 (*k* = 2*n* + 1), unambiguously indicated the space group P2₁/n. The structure was solved by direct methods, and the phosphorus atom was included anisotropically in the structure refinement. All hydrogen atoms were generated in idealized positions but were

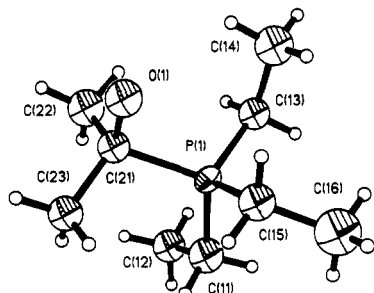
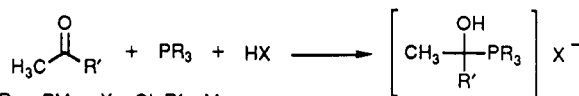
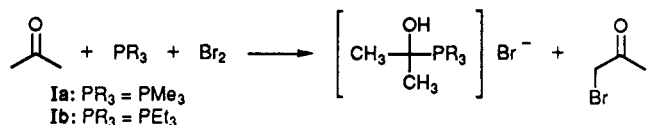


Figure 1. ORTEP drawing of $[(\text{CH}_3)_2\text{C}(\text{OH})\text{PEt}_3]\text{Br}$ showing the atom labeling scheme and 50% probability thermal ellipsoids.

Scheme I



IIa: $\text{PR}_3 = \text{PMe}_3$; X = Cl; $\text{R}' = \text{Me}$

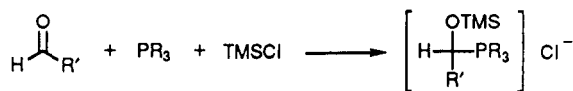
IIb: $\text{PR}_3 = \text{PEt}_3$; X = Cl; $\text{R}' = \text{Me}$

IIIa: $\text{PR}_3 = \text{PMe}_3$; X = *p*- $\text{MeC}_6\text{H}_4\text{SO}_3$; $\text{R}' = \text{Me}$

IIIb: $\text{PR}_3 = \text{PEt}_3$; X = *p*- $\text{MeC}_6\text{H}_4\text{SO}_3$; $\text{R}' = \text{Me}$

Va: $\text{PR}_3 = \text{PMe}_3$; X = Cl; $\text{R}' = \text{H}$

Vb: $\text{PR}_3 = \text{PEt}_3$; X = Cl; $\text{R}' = \text{H}$



TMSCl = $(\text{CH}_3)_3\text{SiCl}$

IVa: $\text{PR}_3 = \text{PMe}_3$; $\text{R}' = \text{C}_6\text{H}_5$

IVb: $\text{PR}_3 = \text{PEt}_3$; $\text{R}' = \text{C}_6\text{H}_5$

not refined. Final atomic positional and isotropic thermal parameters for nonhydrogen atoms are shown in Table III. Bond distances and bond angles are shown in Table IV.

Results and Discussion

While carrying out the bromination of a molybdenum carbonyl complex in the presence of PEt_3 and acetone solvent, a high yield of the unusual addition product $[(\text{CH}_3)_2\text{C}(\text{OH})\text{PEt}_3]\text{Br}$ was obtained. The reaction proceeds in the absence of the metal carbonyl complex, and we reasoned that the $\text{Br}_2/\text{acetone}$ mixture merely serves to generate anhydrous HBr through the bromination of acetone. In fact a variety of 1-hydroxy phosphonium salts (Table I, Scheme I) could be prepared in high yield by the addition of an anhydrous acid to a ketone or aldehyde in the presence of PMe_3 or PEt_3 . No reaction was observed with triphenylphosphine. Tributylphosphine also failed in this reaction, which suggests that insolubility of the product as well as nucleophilicity of the phosphine is important in this reaction. All adducts are white crystalline salts, and those containing triethylphosphine are more hygroscopic than the trimethyl analogues. In the presence of H_2O Ib decomposed to generate PEt_3 , acetone, and HBr , so it is important to maintain anhydrous conditions. The stretching frequencies of OH for phosphonium salts containing PEt_3 have slightly lower values than the PMe_3 analogues, which suggests stronger hydrogen bonding of $\text{O}-\text{H}\cdots\text{Br}$ in the PEt_3 analogues (Table I). It was also possible to trap 1-(trimethylsiloxy) analogues by substituting TMSCl for the anhydrous acid in the synthesis (Scheme I). These compounds may prove useful for the

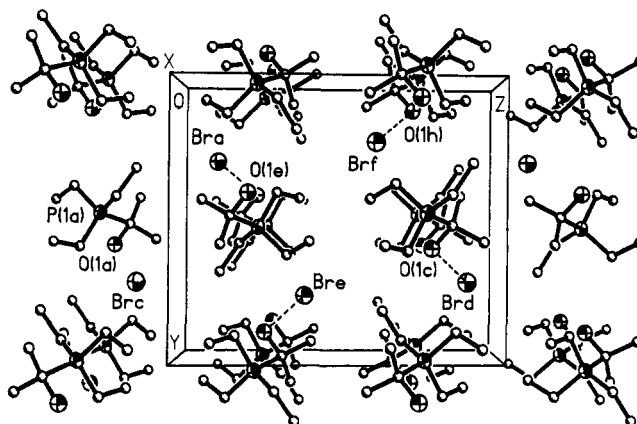
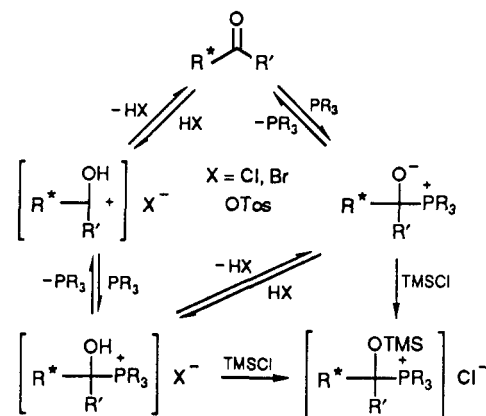


Figure 2. The packing diagram of $[(\text{CH}_3)_2\text{C}(\text{OH})\text{PEt}_3]\text{Br}$ along the *x* axis.

Scheme II



generation of novel Wittig reagents, which donate a $:\text{C}(\text{OTMS})\text{R}$ group.

The molecular structure of Ib is shown in Figure 1. The bond distance to the hydroxylic carbon P(1)–C(21) (1.877 (10) Å) significantly exceeds the other three P–C bond lengths (1.787 (8)–1.808 (8) Å), which may reflect the incipient donor-acceptor character of the bond. The bond distance of C(21)–O(1) (1.429 (10) Å) implies a normal C–O single bond, and the bond angles around C(21) agree with an sp^3 configuration. The C–O distance in Ib resembles that of 1.43 (3) Å found in $\text{Cp}^*\text{Cl}_3\text{Ta}[\eta^2\text{-OC}(\text{PEt}_3)\text{SiMe}_3]$,⁹ but is longer than that of 1.367 (6) Å found in $\text{Cp}(\text{NO})\text{-}(\text{I})\text{Mo}[\eta^2\text{-OC}(\text{PMe}_3)(\text{p-C}_6\text{H}_4\text{Me})]$.¹⁰ These latter metal complexes exhibit reduced P–C bond lengths of 1.81 (3) and 1.831 (5) Å, respectively, to the carbonyl-derived carbon atom when compared to Ib. A packing diagram of Ib (Figure 2) shows a hydrogen bond $\text{O}-\text{H}\cdots\text{Br}$ between O(1) and the Br^- ion of the other molecule related to O(1) by the inversion center. The $\text{O}(1)\cdots\text{Br}$ distance of 3.225 (5) Å is significantly less than the sum of van der Waal's radii.¹⁵

The ^1H NMR spectra of these complexes exhibit diminished couplings between the phosphorus nucleus and α -protons of the hydroxyalkyl group that may be a consequence of the P–C bond lengthening. For example, in IVa and IVb (Table I) the ^{31}P coupling to the α -proton of the $\text{PhCH}(\text{OTMS})$ group is half that of the α -protons of the alkyl substituents. In Va and Vb the ^{31}P coupling to the α -proton of the hydroxyalkyl group could not be resolved. It is unlikely that P–C bond breaking is occurring

(15) Stout, G. H.; Jensen, L. H. *X-ray Structure Determination*; The Macmillan Company: New York, 1968; p 302.

on the NMR time scale because the ^{31}P coupling to the protons of the β -methyl group in Va and Vb was clearly observed. Furthermore, the gated proton decoupled ^{13}C NMR spectrum of Va in $\text{DMSO}-d_6$ showed a dd at δ 61.2 with $^1J_{^{13}\text{C}-\text{H}} = 148$ Hz and $^1J_{^{13}\text{C}-\text{P}} = 61$ Hz for the hydroxylic carbon. This resembles the parameters reported¹⁰ for the "ylid carbon" resonance of $\text{Cp}(\text{NO})(\text{I})\text{Mo}[\eta^2\text{-OC}(\text{PMe}_3)\text{-}(p\text{-C}_6\text{H}_4\text{Me})]$ at δ 72.2 with $^1J_{^{13}\text{C}-\text{P}} = 60.3$ Hz. The silaacyl adduct $\text{Cp}^*\text{Cl}_3\text{Ta}[\eta^2\text{-OC}(\text{PEt}_3)\text{SiMe}_3]$ differs from the preceding examples with a δ 78.0 doublet ($^1J_{^{13}\text{C}-\text{P}} = 7.5$ Hz) observed for the acyl derived carbon; however, P-C couplings to metal bound carbons show a high variability.⁹ A dq at δ 4.6 with $^1J_{^{13}\text{C}-\text{H}} = 133$ Hz and $^1J_{^{13}\text{C}-\text{P}} = 51$ Hz in the spectrum of Va may be assigned to the phosphine methyl groups and a quartet at δ 16.5 with $^1J_{^{13}\text{C}-\text{H}} = 128$ Hz to the remaining methyl group.

Scheme II displays a suggested mechanism for the formation of I-V. It is not clear whether HX or PR_3 addition

to the carbonyl group occurs first, so both possibilities are included in the scheme. Although it is likely that the synthesis of the 1-OTMS derivative occurs by the right-hand path of Scheme II, the possibility of acid catalysis (left path) cannot be excluded.

Acknowledgment. This work is based on research sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under Grant AFOSR-86-0027. We thank the DoD University Research Instrumentation Program (Grant DAAL03-87-G-0071) for funds to purchase an X-ray diffractometer. We thank E. Wenkert and T. D. Tilley for helpful discussions.

Supplementary Material Available: Tables of positional parameters of hydrogen atoms and anisotropic thermal parameters for the phosphorus atom (2 pages); listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

Electrochemical Reduction and Intramolecular Cyclization of 6-Iodo-1-phenyl-1-hexyne at Vitreous Carbon Cathodes in Dimethylformamide

Mohammad S. Mubarak

Department of Chemistry, King Saud University, Abha, Saudi Arabia

Dung D. Nguyen and Dennis G. Peters*

Department of Chemistry, Indiana University, Bloomington, Indiana 47405

Received September 11, 1989

In dimethylformamide containing a tetraalkylammonium perchlorate, a cyclic voltammogram for reduction of 6-iodo-1-phenyl-1-hexyne at a glassy carbon electrode exhibits three prominent waves corresponding to cleavage of the carbon-iodine bond and to subsequent reductions of 1-phenyl-1-hexyne and benzyldenecyclopentane. At potentials for which only reduction of the carbon-iodine bond occurs, large-scale electrolyses of 6-iodo-1-phenyl-1-hexyne afford benzyldenecyclopentane and 1-phenyl-1-hexyne; the yield of the carbocycle, averaging 36%, is insensitive to potential, but the quantity of 1-phenyl-1-hexyne varies from 28 to 48% as the potential is chosen to be more negative. In the presence of diethyl malonate as a proton donor, the quantity of benzyldenecyclopentane changes little, the yield of 1-phenyl-1-hexyne decreases, and substantial (>33%) diethyl (1-phenyl-1-hexyn-6-yl)malonate is obtained. With 1,1,1,3,3,3-hexafluoroisopropyl alcohol as proton source, the yield of benzyldenecyclopentane increases to approximately 60%, whereas the quantity of 1-phenyl-1-hexyne decreases somewhat. It appears that each of the major hydrocarbon products is formed via a combination of one- and two-electron processes.

For a number of years, we have been interested in the electrochemical reduction and intramolecular cyclization of acetylenic halides.¹⁻⁴ In dimethylformamide containing tetra-*n*-butylammonium perchlorate, electrolysis of a low concentration (<1 mM) of 6-chloro-1-phenyl-1-hexyne at a mercury cathode¹ proceeds via reduction of the carbon-carbon triple bond to yield a radical anion that cyclizes with displacement of chloride to afford predominantly benzyldenecyclopentane; however, at a higher concentration (>2 mM), the acetylenic chloride undergoes extensive electrolytically induced, base-catalyzed rearrangement to 6-chloro-1-phenyl-1,2-hexadiene, and reduction of the allene leads to formation of a number of carbocyclic and acyclic species, the two principal products being 1-benzylcyclopentane and benzyldenecyclopentane.

Unlike the behavior of 6-chloro-1-phenyl-1-hexyne, the reductions of 6-iodo- and 6-bromo-1-phenyl-1-hexyne at

mercury in dimethylformamide containing tetra-*n*-butylammonium perchlorate² initially involve one-electron scission of the carbon-halogen bond and are complicated by the formation of substantial amounts of diorganomercury compounds. Benzyldenecyclopentane, the desired product, can be obtained in a yield no higher than 24% from the acetylenic iodide, and the quantity of this carbocycle declines as the potential is made more negative.

Reduction of 1-iodo- and 1-bromo-5-decyne has been examined with the aid of both mercury³ and carbon⁴ electrodes in dimethylformamide containing several different tetraalkylammonium perchlorates. Because these starting materials possess no phenyl-conjugated acetylenic bond, the only electrochemically reducible site is the carbon-halogen moiety. At potentials for which the 5-

(2) Willett, B. C.; Moore, W. M.; Salajegheh, A.; Peters, D. G. *J. Am. Chem. Soc.* 1979, 101, 1162-1167.

(3) Shao, R.-L.; Cleary, J. A.; La Perriere, D. M.; Peters, D. G. *J. Org. Chem.* 1983, 48, 3289-3294.

(4) Shao, R.-L.; Peters, D. G. *J. Org. Chem.* 1987, 52, 652-657.

(1) Moore, W. M.; Salajegheh, A.; Peters, D. G. *J. Am. Chem. Soc.* 1975, 97, 4954-4960.