Simple Preparation of (2,2′-Biphenylylene)phenylphosphine Oxide and Role of Triphenylphosphine Oxide as a Mediator for Formation of Biaryl Derivatives

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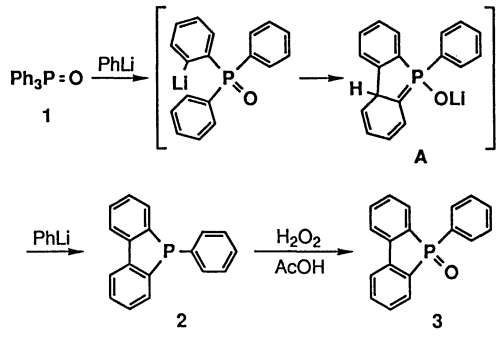
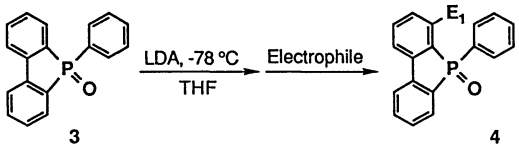
Synopsis. (2,2′-Biphenylylene)phenylphosphine oxide (**3**) was prepared simply by the reaction of triphenylphosphine oxide (**1**) with phenyllithium and subsequently with aqueous hydrogen peroxide in acetic acid. The oxide **3** reacted with lithium diisopropylamide (LDA) and then with several electrophiles to afford regiospecifically ortho-substituted compounds in moderate yields, which were converted to unsymmetrical 2- and 2,3′-substituted 1,1′-biaryls and triphenylphosphine oxide (**1**).

Although numerous phosphines have been utilized in modern organic synthesis, i.e., as starting materials for Wittig reagents[1] and ligands for transition metals,[2] phosphine oxides have been investigated a little and considered as undesired end products for the reactions. The P=O bond energy of triphenylphosphine oxide (**1**) is quite high (130 kcal) and is hardly reduced by simple reducing reagents.[3] This might prevent the utilization of **1** in organic synthesis. Recently, we found that triarylphosphine oxides, diaryl sulfoxides, and diaryl selenoxides underwent facile ligand exchange by the reactions with organolithium reagents.[4] On the other hand, we reported a new ortho-lithiation reaction of diaryl sulfoxides.[5] In the course of studies on the reactions of oxides derived from heteroatom (group 15 or 16 elements)-containing compounds with organolithium or Grignard reagents, we found that the ring closure reaction of triphenylphosphine oxide (**1**) on treatment with phenyllithium took place together with elimination of the oxygen atom to afford (2,2′-biphenylylene)phenylphosphine (**2**) in moderate yield. In this note, we report simple preparation of (2,2′-biphenylylene)phenylphosphine oxide (**3**) and its application for the synthesis of unsymmetrical biaryls. We also emphasize that **1** works as a mediator for the synthesis of biaryls.

When **1** was allowed to react with phenyllithium in refluxing tetrahydrofuran (THF), (2,2′-biphenylylene)-phenylphosphine (**2**) was obtained in 65% yield. Then **2** was treated with aqueous hydrogen peroxide in acetic acid to afford (2,2′-biphenylylene)phenylphosphine oxide (**3**) in 93% yield. In the reaction of **1** with phenyllithium intramolecular carbon-carbon bond formation at the ortho-positions of the two phenyl rings and reduction of phosphine oxide to phosphine took place simultaneously. Although it is hardly to argue the reaction mechanism, the following mechanism involving initial proton abstraction by phenyllithium then the incipient formation of **A** which was also suggested in the reaction of tetraphenylphosphonium salt with organolithium reagents[6] could be the probable process as shown in Scheme 1. Apparently, when one used two equivalents of phenyllithium, **2** was obtained in highest yield, namely, the reactions of **1** with one and two equivalents of phenyllithium gave **2** in 11 and 65% yields respectively. When **3** was treated with LDA and then with electrophiles at −78 °C, lithiation took place regiospecifically at the 3-position in the biphenyl ring to give monosubstituted compounds **4** in moderate yields as shown in Scheme 2 and Table 1. These 3-substituted (2,2′-biphenylylene)phenylphosphine oxides **4** reacted with phenyllithium to give the corresponding substitution products **5** in moderate yields. However, the second electrophile could not be introduced at the 2′-position in the biphenyl ring. These results seem to indicate that in the reactions of lithiated **4** with electrophiles the steric or electronic effect by the one substituent at the 3′-position prevents the approach for the second electrophile at the 2′-position. Although two substituents could not be introduced in one phenyl ring of biphenyl, **5** reacted initially with phenyllithium and subsequently with electrophiles to afford 2,3′-disubstituted 1,1′-biaryls **6** and triphenylphosphine oxide (**1**) in good yields as shown in Scheme 3 and Table 2. The recovered **1** can be used again as a starting material for



Scheme 1.



Scheme 2.

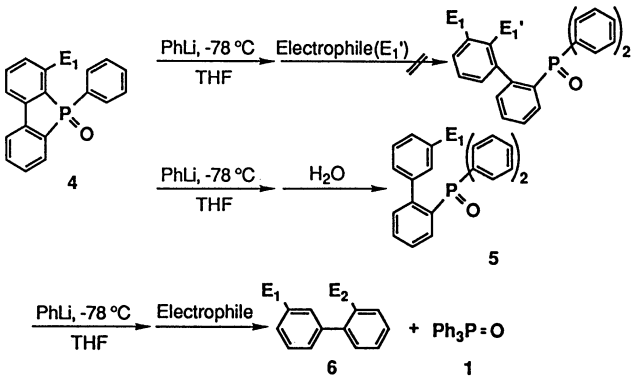
Table 1. Reactions of (2,2-Biphenylylene)phenylphosphine Oxide (**3**) with LDA and Electrophiles

LDA equiv	Electrophile	E_1	Yield/% **4**
1.0	$(CH_3)_3SiCl$	$(CH_3)_3Si$	52 (**4a**)[a]
1.0	PhCHO	PhCH(OH)	21 (**4b**)
1.0	CH_3CHO	$CH_3CH(OH)$	53 (**4c**)

a) Small amount of disubstituted product was obtained.

Table 2. Reactions of Phosphine Oxides **3** and **4a** with Phenyllithium and Electrophiles

Phosphine Oxide E_1	Yield/% **5**	Electrophile	E_2	Yield/% **6**	Yield/% **1**
H (**3**)	95 (**5a**)	—	H	69 (**6a**)	60
		$(CH_3)_3SiCl$	$(CH_3)_3Si$	46 (**6b**)	65
		PhCHO	PhCH(OH)	79 (**6c**)	62
		CH_3CHO	$CH_3CH(OH)$	55 (**6d**)	63
$(CH_3)_3Si$ (**4a**)	47 (**5b**)	—	H	99 (**6e**)	95
		$(CH_3)_3SiCl$	$(CH_3)_3Si$	16 (**6f**)	49
		CH_3CHO	$CH_3CH(OH)$	54 (**6g**)	84



Scheme 3.

the simple reaction system to prepare unsymmetrical biaryls **6** and hence **1** plays a role of a mediator for the system. These procedures can expand the scope for the syntheses of unsymmetrical biaryls.

Experimental

All melting points are uncorrected. IR spectra were recorded on a JASCO FT/IR-5000 spectrometer. NMR spectra were obtained with a Hitachi R-600, a JEOL EX 270, or a Bruker AM-500. Mass spectra were taken with a Hitachi RMU-6MG, a Shimadzu GCMS QP-2000A, or a JEOL JMS-SX 102 mass spectrometer. Elemental analyses were carried out by Chemical Analysis Center at this University. All reagents were obtained from Wako Pure Chemical Industries, Ltd. or Aldrich Chemical Co. The reaction solvents were further purified by general methods.

Synthesis of (2,2′-Biphenylylene)phenylphophine (2). To a stirred solution of **1** (2.8 g, 10.0 mmol) in THF (80 mL) at 0 °C under N_2 atmosphere was added 1.8 M (1 M=1 mol dm^{-3}) phenyllithium (11.2 mL, 20.1 mmol). The mixture was refluxed for 12 h. After hydrolysis, the solvent was removed under reduced pressure. To the residue was added water (100 mL) and the mixture was neutralized with 1 M hydrochloric acid, extracted with dichloromethane (3×100 mL). The extract was dried with anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, hexane–ethyl acetate=4 : 1) to give phosphine **2** in 65% yield. Recrystallization from ethyl acetate gave colorless crystals; mp 92—93 °C (lit,[7] 93—94 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ=7.18—7.25 (m, 3H, 3,4,5-PhH), 7.27—7.31 (m, 4H, 5,5′,6,6′-BiphH), 7.43 (t, J=7.8 Hz, 2H, 4,4′-BiphH), 7.66—7.71 (m, 2H, 2,6-PhH), 7.92 (d, J=7.8 Hz, 2H, 3,3′-BiphH); ^{31}P NMR (109 MHz, $CDCl_3$) δ=−11.6; MS m/z 260 (M^+).

Synthesis of (2,2′-Biphenylylene)phenylphosphine Oxide (3). To a stirred solution of **2** (260 mg, 1.0 mmol) in acetic acid (30 mL) was added 30% aqueous hydrogen peroxide (0.0168 mL, 1.47 mmol). The mixture was stirred at room temperature for 3 h, and the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (40 mL) and washed with saturated aqueous sodium hydrogencarbonate (3×30 mL) and saturated aqueous sodium chloride (2×30 mL). The organic layer was dried with anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was recrystallized with ethyl acetate to give phosphine oxides **3** as colorless crystals in 93% yield. Mp 159—162 °C (lit,[8] 162—164.5 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ=7.37 (t, J=7.5 Hz, 2H, 4,4′-BiphH), 7.38 (t, J=7.3 Hz, 2H, 3,5-PhH), 7.48 (t, J=7.3 Hz, 1H, 4-PhH), 7.58 (t, J=7.5 Hz, 2H, 5,5′-BiphH), 7.65 (dd, J_{PCCH}=12.8, J=7.3 Hz, 2H, 2,6-PhH), 7.71 (dd, J_{PCCCH}=8.6, J=7.5 Hz, 2H, 6,6′-BiphH), 7.82 (dd, J_{PCCH}=2.9, J=7.5 Hz, 2H, 3,3′-BiphH); ^{31}P NMR (109 MHz, $CDCl_3$) δ=32.2; IR (KBr) 1195 cm^{-1} (PO); MS m/z 276 (M^+).

Reactions of (2,2′-Biphenylylene)phenylphosphine Oxide (3) with LDA and Electrophiles. To a stirred solution of **3** (276 mg, 1.0 mmol) in THF (10 mL) was added 0.17 M LDA (6.0 mL, 1.0 mmol) in THF solution under N_2 atmosphere at −78 °C for 3 h. To the mixture was added trimethylsilyl chloride (0.30 mL, 2.4 mmol) and the mixture was stirred at −78 °C for 3 h. After hydrolysis, the solvent was removed under reduced pressure. To the residue was added water (40 mL) and the mixture was neutralized with 1 M hydrochloric acid, extracted with dichloromethane (3×40 mL). The extract was dried with anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, ethyl acetate) to give **4a** in 52% yield. Recrystallization from hexane–ethyl acetate gave colorless crystals; mp 189—190 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.17 (s, 9H, CH_3), 7.29—7.86 (m, 12H, PhH, BiphH); ^{13}C NMR (125 MHz, $CDCl_3$) δ=0.0 (s), 120.8 (d, ^2J=9.8 Hz), 121.5 (d, ^2J=10.0 Hz), 128.6 (d, ^3J=12.3 Hz), 129.1 (d, ^3J=9.6 Hz), 129.3 (d, ^3J=10.8 Hz), 131.0 (d, ^3J=12.3 Hz), 131.4 (d, ^4J=2.6 Hz), 131.8 (d, ^4J=2.7 Hz), 132.6 (d, ^1J=106.7 Hz), 132.9 (s), 133.1 (d, ^1J=106.7 Hz), 135.8 (d, ^3J=14.0 Hz), 137.6 (d, ^1J=108.8 Hz), 140.6 (d, ^2J=21.6 Hz), 142.5 (d, ^2J=24.8 Hz), 145.7 (d, ^2J=16.3 Hz); ^{31}P NMR (109 MHz, $CDCl_3$) δ=32.9; IR (KBr) 1207 cm^{-1} (PO); MS m/z 348 (M^+). Found: C, 72.22; H, 6.06%. Calcd for $C_{21}H_{21}OPSi$: C, 72.38; H, 6.07%. Phosphine oxides **4b** and **4c** were obtained as two diastereomers by the same procedure as **4a**.

4b: One diastereomer; colorless crystals; mp 258—260 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ=6.00 (s, 1H, CH), 6.99—7.00 (m, 1H, 2′-ArH), 7.12—7.14 (m, 2H, 3′,5′-ArH), 7.19—7.22 (m, 2H, 4′,6′-ArH), 7.35—7.41 (m, 4H, 4,4′,6,6′-BiphH), 7.48 (t, J=7.4 Hz, 1H, 4-PhH), 7.59—7.65 (m, 2H, 5,5′-BiphH), 7.64 (d, J_{PCCH}=12.9 Hz, 1H, 3′-BiphH), 7.68 (t, J=7.4 Hz, 2H, 3,5-PhH), 7.79 (dd, J_{PCCH}=47.2 Hz, J=7.4 Hz, 2H, 2,6-PhH); ^{31}P NMR (109 MHz, $CDCl_3$) δ=35.8; IR (KBr) 3206 (OH), 1185 cm^{-1} (PO). Found: m/z 382.1136. Calcd for $C_{25}H_{19}O_2P$: M, 382.1123.

The other diastereomer; colorless crystals; mp 240—242.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ=6.05 (s, 1H, CH), 7.05—7.07 (m, 2H, 2',6'-ArH), 7.08—7.09 (m, 1H, 4'-ArH), 7.15—7.17 (m, 2H, 3',5'-ArH), 7.25—7.27 (m, 2H, 4,4'-BiphH), 7.34 (d, J=7.2 Hz, 2H, 6,6'-BiphH), 7.38 (t, J=7.8 Hz, 1H, 4-PhH), 7.44 (d, J=7.2 Hz, 1H, 5-BiphH), 7.46 (d, J=7.2 Hz, 1H, 5'-BiphH), 7.55 (d, J=7.8 Hz, 2H, 3,5-PhH), 7.61 (d, J_{PCCH}=15.0 Hz, 1H, 3'-BiphH), 7.79 (dd, J_{PCCH}=28.2 Hz, J=7.8 Hz, 2H, 2,6-PhH); ^{31}P NMR (109 MHz, $CDCl_3$) δ=35.7; IR (KBr) 3258 (OH), 1180 cm^{-1} (PO). Found: m/z 382.1112. Calcd for $C_{25}H_{19}O_2P$: M, 382.1123.

4c: One diastereomer; colorless crystals; mp 214—215.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ=1.36 (d, J=6.5 Hz, 3H, CH_3), 5.10 (q, J=6.5 Hz, 1H, CH), 7.33—7.35 (m, 2H, 4,4'-BiphH), 7.37—7.39 (m, 2H, 6,6'-BiphH), 7.46 (t, J=7.5 Hz, 1H, 4-PhH), 7.54—7.58 (m, 2H, 5,5'-BiphH), 7.62 (d, J_{PCCH}=12.4 Hz, 1H, 3'-BiphH), 7.64 (t, J=7.5 Hz, 2H, 3,5-PhH), 7.78 (dd, J_{PCCH}=33.8, J=7.5 Hz, 2H, 2,6-PhH); ^{31}P NMR (109 MHz, $CDCl_3$) δ=34.4; IR (KBr) 3292 (OH), 1193 cm^{-1} (PO). Found: m/z 320.0928. Calcd for $C_{20}H_{17}O_2P$: M, 320.0966.

The other diastereomer; colorless crystals; mp 222.5—224.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ=1.30 (d, J=6.2 Hz, 3H, CH_3), 5.06 (q, J=6.2 Hz, 1H, CH), 7.36—7.39 (m, 4H, 4,4',6,6'-BiphH), 7.47 (t, J=7.8 Hz, 1H, 4-PhH), 7.55—7.58 (m, 2H, 5,5'-BiphH), 7.61 (d, J_{PCCH}=12.4 Hz, 1H, 3'-BiphH), 7.64 (t, J=7.8 Hz, 2H, 3,5-PhH), 7.78 (dd, J_{PCCH}=45.9, J=7.8 Hz, 2H, 2.6-PhH); ^{31}P NMR (109 MHz, $CDCl_3$) δ=34.9; IR (KBr) 3296 (OH), 1185 cm^{-1} (PO). Found: m/z 320.0937. Calcd for $C_{20}H_{17}O_2P$: M, 320.0966.

Reactions of (2,2'-Biphenylylene)phenylphosphine Oxide (3) and [(3-Trimethylsilyl)-2,2'-biphenylylene]phenylphosphine Oxide (4a) with Phenyllithium. In a typical run, to a stirred solution of **3** (276 mg, 1.0 mmol) in THF (15 mL) at −78 °C under N_2 atmosphere was added 1.8 M phenyllithium (0.8 mL, 1.5 mmol). The mixture was stirred at −78 °C for 30 min. After hydrolysis, the solvent was removed under reduced pressure. To the residue was added water (30 mL) and the mixture was neutralized with 1 M hydrochloric acid, extracted with dichloromethane (3×30 mL). The extract was dried with anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, dichloromethane, ethyl acetate) to give **5a** in 95% yield. Recrystallization from ethyl acetate gave colorless crystals; mp 148.5—150 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ=7.01—7.58 (m, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ=126.5 (d, ^3J=12.3 Hz), 127.1 (s), 127.2 (s), 128.0 (d, ^3J=12.0 Hz), 130.1 (s), 131.1 (d, ^4J=2.2 Hz), 131.5 (d, ^2J=9.4 Hz), 131.7 (s), 131.7 (d, ^1J=101.1 Hz), 131.9 (d, ^2J=10.1 Hz), 133.1 (d, ^1J=103.6 Hz), 134.0 (d, ^3J=12.1 Hz), 140.3 (d, ^3J=4.4 Hz), 147.7 (d, ^2J=8.9 Hz); ^{31}P NMR (109 MHz, $CDCl_3$) δ=26.3; IR (KBr) 1191 cm^{-1} (PO); MS m/z 354 (M^+). Found: C, 81.15; H, 5.40%. Calcd for $C_{24}H_{19}OP$: C, 81.34; H, 5.40%.

5b: Colorless crystals; mp 137.5—138.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.14 (s, 9H, CH_3), 7.05—7.57 (m, 18H, ArH); ^{13}C NMR (125 MHz, $CDCl_3$) δ=−1.1 (s), 126.6 (d, ^3J=12.3 Hz), 126.7 (s), 128.0 (d, ^3J=11.7 Hz), 130.7 (s), 131.0 (d, ^4J=2.7 Hz), 131.6 (d, ^2J=9.1 Hz), 131.6 (d, ^1J=100.0 Hz), 131.7 (d, ^4J=2.3 Hz), 132.0 (d, ^2J=10.0 Hz), 132.1 (s), 133.0 (d, ^1J=104.0 Hz), 134.2 (d, ^3J=12.0 Hz), 134.7 (s), 139.1 (s), 139.7 (d, ^3J=3.8 Hz), 147.9 (d, ^2J=9.0 Hz); ^{31}P NMR (109 MHz, $CDCl_3$) δ=27.1; MS m/z 426 (M^+). Found: C, 75.97; H, 6.55%. Calcd for $C_{27}H_{27}OPSi$: C, 76.02; H, 6.38%.

Reactions of (2-Biphenylyl)diphenylphosphine Oxide (5a) and [3'-(Trimethylsilyl)-2-biphenylyl]diphenylphosphine Oxide (5b) with Phenyllithium. In a typical run, to a stirred solution of **5a** (200 mg, 0.6 mmol) in THF (10 mL) was added 1.8 M phenyllithium (1.0 mL, 1.8 mmol) in THF solution under N_2 atmosphere at −78 °C for 30 min. To the mixture was added acetaldehyde (0.05 mL, 0.9 mmol) and the mixture was stirred at −20 °C for 3 h. After hydrolysis, the solvent was removed under reduced pressure. To the residue was added water (30 mL) and the mixture was neutralized with 1 M hydrochloric acid, extracted with dichloromethane (3×30 mL). The extract was dried with anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (silica gel; eluent, hexane–ethyl acetate=1 : 2) to give 2-(1-hydroxyethyl)biphenyl (**6d**) and **1** in 55% and 63% yields respectively.

6d: Mp 105—107 °C (lit,[9] 111—112 °C); ^{1}H NMR ($CDCl_3$) δ=1.40 (d, J=6.6 Hz, 3H, CH_3), 4.98 (q, J=6.6 Hz, 1H, CH), 7.21—7.62 (m, 9H, ArH); IR (KBr) 3252 cm^{-1} (OH); MS m/z 198 (M^+). Found: C, 84.66; H, 7.12%. Calcd for $C_{14}H_{14}O$: C, 84.81; H, 7.12%.

6b: Colorless liquid; ^{1}H NMR ($CDCl_3$) δ=0.00 (s, 9H, CH_3), 7.15—7.70 (m, 9H, ArH); MS m/z 226 (M^+). Found: C, 79.17; H, 7.96%. Calcd for $C_{15}H_{18}Si$: C, 79.58; H, 8.01%.

6c: Mp 144—145 °C (lit,[10] 146—147 °C); ^{1}H NMR ($CDCl_3$) δ=5.93 (s, 1H, CH), 7.18—7.56 (m, 14H, ArH); IR (KBr) 3358 cm^{-1} (OH); MS m/z 260 (M^+).

6e: Colorless liquid; ^{1}H NMR ($CDCl_3$) δ=0.18 (s, 9H, CH_3), 7.30—8.90 (m, 9H, ArH); MS m/z 266 (M^+). Found: C, 79.71; H, 8.09%. Calcd for $C_{15}H_{18}Si$: C, 79.58; H, 8.01%.

6f: Colorless liquid; ^{1}H NMR ($CDCl_3$) δ=0.29 (s, 9H, CH_3), 0.35 (s, 9H, CH_3), 7.27—7.46 (m, 8H, ArH). Found: m/z 298.1539. Calcd for $C_{18}H_{26}Si_2$: M, 298.1573.

6g: Colorless liquid; ^{1}H NMR ($CDCl_3$) δ=0.28 (s, 9H, CH_3), 1.44 (d, J=6.6 Hz, 3H, CH_3), 4.44 (q, J=6.6 Hz, CH), 7.21—7.62 (m, 8H, ArH); IR (KBr): 3294 cm^{-1} (OH); MS m/z 270 (M^+). Found: C, 75.79; H, 8.38%. Calcd for $C_{17}H_{22}OSi$: C, 75.50; H, 8.20%.

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References

1) G. Wittig, *Angew. Chem.*, **68**, 505 (1956); H. J. Bestmann and R. Zimmermann, "Organic Phosphorus Compounds," ed by G. M. Kosolapoff and L. Maier, John Wiley and Sons, New York (1972), Chap. 5A.

2) G. Booth, "Organic Phosphorus Compounds," ed by G. M. Kosolapoff and L. Maier, John Wiley and Sons, New York (1972), Chap. 3A; J. G. Verkade and K. J. Coskran, Chap. 3B.

3) K. Naumann, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **91**, 7012 (1969); L. Horner and W. D. Balzer, *Tetrahedron Lett.*, **1965**, 1157; H. Fritzsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, **97**, 1988 (1964); L. Horner, H. Hoffmann, and P. Beck, *ibid.*, **91**, 1583 (1958); F. Hein, K. Issleib, and H. Rabold, *Z. Anorg. Allg. Chem.*, **287**, 208 (1956); K. Issleib and G. Grams, *ibid.*, **299**, 58 (1959).

4) N. Furukawa, "Heteroatom Chemistry," ed by E. Block, Verlag, New York (1990), p. 165; N. Furukawa, S. Ogawa, K. Matsumura, and H. Fujihara, *J. Org. Chem.*, in press.

5) S. Ogawa and N. Furukawa, *J. Org. Chem.*, in press.

6) D. Seyferth, W. B. Hughes, and J. K. Heeren, *J. Am. Chem. Soc.*, **87**, 3467 (1965).

7) G. Wittig and A. Maercker, *Chem. Ber.*, **97**, 747 (1964).

8) G. Wittig and G. Geissler, *Justus Liebigs Ann. Chem.*, **580**, 44 (1953).

9) W. F. Huber, M. Renoll, A. G. Rossow, and D. T. Mowry, *J. Am. Chem. Soc.*, **68**, 1109 (1946).

10) G. W. Gribble and R. M. Leese, *Synthesis*, **1977**, 172.