

76SF00098. Structures were done by Michael Waldyke using a program written by Michael Miller for the Tektronix 4050 series.

Registry No. 1, 265-49-6; 2, 23709-78-6; 4, 87532-97-6; 5,

87532-98-7; 6, 87532-99-8; 7, 87533-00-4; 8, 87532-96-5; 9, 87555-25-7; 11, 87533-01-5; DDQ, 84-58-2; UCl<sub>4</sub>, 10026-10-5; ThCl<sub>4</sub>, 10026-08-1; COT, 629-20-9; K<sub>2</sub>COT, 29590-71-4; bromocyclooctatetraene, 7567-22-8; 1,4-dibromobutane, 110-52-1; 1,3-butadiene, 106-99-0.

## A Facile Synthesis of 1,2-Bis(phosphino)benzene and Related Alkylated Species

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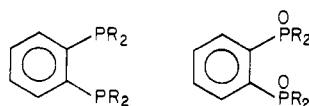
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Photolysis of 1,2-dichlorobenzene in trimethyl phosphite at 60 °C for 5 days gives 1,2-bis(dimethoxyphosphoryl)benzene (**3**) in 50% yield. The reaction can be carried out on a multimolar scale. Species **3** is reduced to 1,2-bis(phosphino)benzene (**4**) in 83% yield following distillation, utilizing a reagent derived from trimethylsilyl chloride and lithium aluminum hydride in THF. Diphosphine **3** may be transformed in high yields into 1,2-bis(methylphosphino)-, 1,2-bis(dimethylphosphino)-, and 1,2-bis(2-propylphosphino)benzene using deprotonation/alkylation techniques.

### Introduction

Reactions that create carbon-phosphorus bonds, especially those which produce two such bonds in the same molecule, have been of considerable interest to coordination and organometallic chemists for years. Particularly attractive are reactions that give 1,2-disubstituted benzenes **1** since these species are "preorganized" entropically for



1, R = H, alkyl, aryl

2

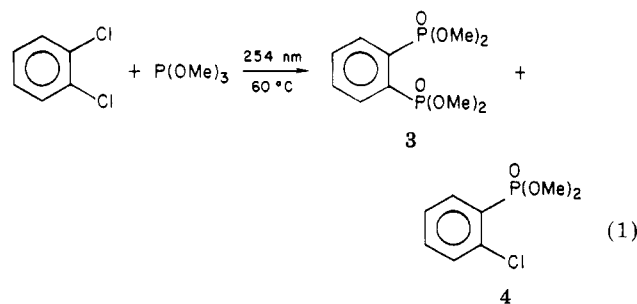
chelation of transition metals. A number of routes have been described to obtain **1** directly from aromatic precursors, all of which suffer from difficulty of manipulation, separation of complex mixtures, and low yields.<sup>1</sup> In particular, an efficient, relatively inexpensive synthesis that yields **1** (R = Me) in high purity has remained a challenge for two decades.<sup>1a-c,f,g</sup> Several routes have been developed to the dioxygenated species **2**. One type of reaction involves the substitution of phosphoryl moieties for halogen by using a photocatalyzed reaction of dialkyl phosphite anions<sup>2</sup> or a photocatalyzed<sup>3</sup> or Ni(II)-catalyzed<sup>4</sup> reaction of trialkyl phosphites with 1,2-dihalogenated benzenes. An alternative route to **2** involves a Diels-Alder reaction of a diphosphorylalkyne with a cyclic diene, followed by expulsion of a small molecule concomitant with aromatization.<sup>5</sup>

Although compounds **2** appear to be somewhat more

easily accessible than a direct route to **1**, there remains the nontrivial problem of reduction of **2** to **1**. This report describes the relatively inexpensive and facile synthesis of **3** and thence to **5-7**.

### Results and Discussion

The photochemical reaction of 1-iodo-2-bromobenzene with trimethyl phosphite has been reported to give **3** in 87% yield.<sup>3</sup> The same reaction with 1-iodo-2-chlorobenzene gave **3** in 28% yield, and no reaction was reported with 1,2-dichlorobenzene. Since the 1-iodo-2-halobenzenes are expensive,<sup>6</sup> we reinvestigated the reaction with 1,2-dichlorobenzene. When the photolysis is carried out at 60 °C for 5 days, **3** is formed in about 50% yield, along with **4** (20%, eq 1). After removal of the reactants under



vacuum, **3** and **4** are separated by recrystallization. The reaction may be carried out routinely on a 3.5-mol scale of the limiting reagent (Cl<sub>2</sub>C<sub>6</sub>H<sub>4</sub>) to give about 500-g quantities of purified **3** per run.

The reduction of **3** to **5** proved to be considerably more challenging than might have been expected from a perusal of the pertinent literature.<sup>7</sup> Reaction of **3** with LiAlH<sub>4</sub>

(1) Inter alia: (a) Chatt, J.; Hart, F. A. *J. Chem. Soc.* 1960, 1738. (b) Hart, F. A. *Ibid.* 1960, 3324. (c) Clark, R. J. H.; Negrotti, R. H. V.; Nyholm, R. S. *Chem. Commun.* 1966, 486. (d) Hartley, J. G.; Venanzi, L. M.; Goodall, D. C. *Ibid.* 1963, 3930. (e) Quin, L. D.; Humphrey, J. S., Jr. *J. Am. Chem. Soc.* 1961, 83, 4124. (f) Meiners, J. H.; Verkade, J. G. *J. Coord. Chem.* 1977, 7, 131. (g) Warren, L. F.; Bennett, M. A. *J. Am. Chem. Soc.* 1974, 96, 3340. (h) Warren, L. F.; Bennett, M. A. *Inorg. Chem.* 1976, 15, 3126 and references therein.

(2) Bard, R. R.; Bunnett, J. F.; Traber, R. P. *J. Org. Chem.* 1979, 44, 4918.

(3) Obrycki, R.; Griffin, C. E. *Tetrahedron Lett.* 1966, 5049.

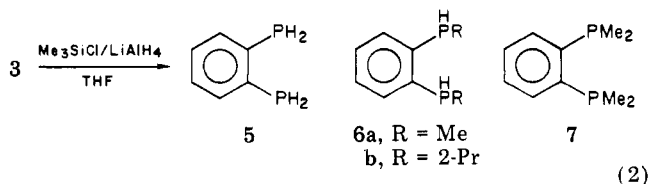
(4) Tavs, P. *Chem. Ber.* 1970, 103, 2428.

(5) (a) Kyba, E. P.; Rines, S. P.; Owens, P. W.; Chou, S.-S. P. *Tetrahedron Lett.* 1981, 22, 1875. In this paper we neglected to acknowledge a previously published paper that outlined chemistry very similar to ours: (b) Seyferth, D.; Paetsch, J. D. H. *J. Org. Chem.* 1969, 34, 1483.

(6) E.g.: 1-bromo-2-iodobenzene is available from Aldrich Chemical Co. at 5 g/\$19.25.

in THF at reflux gave **6a** (16%) as the only isolable product, presumably by the reaction of **5** or its anion with **3** as a methylating agent. If the reaction were carried out at  $-78^{\circ}\text{C}$ , **5** could be obtained in ca. 23% yield, but the sample contained about 5% impurities by  $^{31}\text{P}$  NMR spectroscopy. A much cleaner product could be obtained by the use of the tetraisobutyl ester corresponding to **3**, obtained from **3** by ester exchange, albeit in only 25% yield. Other hydride reagents [e.g., bis(2-methoxyethoxy)aluminum hydride, lithium triethylborohydride] under a variety of conditions gave similar or worse results. The reaction of **3** with diphenylsilane under conditions reported<sup>8</sup> to give high yields of primary phosphines starting with dialkyl phosphonates proved to be impossible to control and gave myriad products.

The reduction problem was finally solved with a unique combination of reagents, trimethylsilyl chloride/lithium aluminum hydride in a 1:1 molar ratio (1:4 silicon-hydride). Reaction of this mixture with **3** led to the clean production of **5** in 83% isolated yield (eq 2). The spectral properties agreed with those reported.<sup>9</sup>



Substrate **5** is a convenient starting material for 1,2-bis(alkylphosphino)- and 1,2-bis(dialkylphosphino)-benzenes. Treatment of **5** in THF with 2 equiv of *n*-BuLi at  $-78^{\circ}\text{C}$ , followed by the addition of 2 equiv of methyl iodide gave **6a** as a mixture of meso and *dl* isomers in 83% isolated yield. Species **6a** may be transformed similarly into **7** in 90% yield after distillation.

We have extended this chemistry to a secondary alkylating agent, 2-bromopropane, in which there existed the question of the facility of a competing E2 reaction. Treatment of **5** with 2 equiv of *n*-BuLi at  $-78^{\circ}\text{C}$ , followed by the addition of a cold ( $-25^{\circ}\text{C}$ ) THF solution of 2-bromopropane, followed by a standard workup gave impure **6b** in 74% yield after distillation. The impurities were the mono- and trialkylated materials (ca. 8% each); thus this alkylation is less selective than that with methyl iodide. There appeared to be little evidence for an elimination reaction, judging from the amount of isolated product, although no attempt was made to detect propene.

## Experimental Section

**General Information.** Proton magnetic resonance spectra were obtained on a Varian EM-390 or a Varian FT-80 spectrometer. Carbon-13 and proton-decoupled phosphorus-31 NMR spectra were determined on a Varian FT-80 spectrometer at 20.1 and 32.4 MHz, respectively. Chemical shifts are given in parts per million relative to  $\text{Me}_4\text{Si}$  for  $^{13}\text{C}$  and relative to 85%  $\text{H}_3\text{PO}_4$  for  $^{31}\text{P}$  NMR spectra. Chemical shifts upfield of the standard are defined as negative.

Unless noted, all of the reactions, manipulations, and purification steps involving phosphines were performed under a dry nitrogen or argon atmosphere. Air-sensitive liquids were transferred by Teflon flexneedles by using nitrogen pressure or by

syringe. All concentrations of solutions were carried out on a rotary evaporator under water aspiration pressures unless otherwise noted. Solutions were dried with anhydrous magnesium sulfate.

The photochemical apparatus was an Ace Glass, Inc., 2-L reactor equipped with a 550-W Conrad-Hanovia medium-pressure mercury vapor lamp and quartz immersion well.

**1,2-Bis(dimethoxyphosphoryl)benzene (3).** A solution of trimethyl phosphite (1421 g, 11.5 mol) and 1,2-dichlorobenzene (522 g, 3.55 mol) was photolyzed at  $60^{\circ}\text{C}$  for 134 h. (It was necessary to wipe clean the immersion well several times during this period.) The mixture was concentrated by distillation under vacuum by using a capillary ebullator. The distillate was a mixture of starting materials that could be recycled. The residue was cooled to  $-20^{\circ}\text{C}$  overnight and filtered to give crude **3** (266 g). The oily filtrate (626 g) that was a 1:1 mixture (by  $^{31}\text{P}$  NMR) of **3** and **4** was dissolved in acetone (2 L) and cooled to  $-20^{\circ}\text{C}$  to give an additional amount of crude **3** (300 g). The combined portions of crude **3** were recrystallized from acetone-ether to give pure **3** (495 g, 47%), as a white crystalline solid, mp  $79-81^{\circ}\text{C}$  (lit.<sup>3</sup> mp  $80-81^{\circ}\text{C}$ ). The mother liquors from the purification of **3** were highly enriched in **4**, and these were recycled in the photochemical reaction to give additional amounts of **3**.

**1,2-Bis(phosphino)benzene (5).** Trimethylsilyl chloride (44.5 g, 410 mmol) was added to a stirred solution of lithium aluminum hydride (15.6 g, 410 mmol) in THF (200 mL) at  $-78^{\circ}\text{C}$ . The resulting mixture was allowed to warm to room temperature and stirred for 2 h. A solution of **3** (20.0 g, 68.0 mmol) in THF (200 mL) was then added to the reducing mixture at  $-30^{\circ}\text{C}$ . The resulting mixture was allowed to warm to room temperature and stirred for 36 h. Water (100 mL) followed by 1 N aqueous sodium hydroxide was added, and the two layers were separated. The aqueous layer was extracted with diethyl ether ( $2 \times 200$  mL), and the combined organic extracts were dried and concentrated. Distillation of the residue gave **5** as a colorless, air-sensitive liquid (8.0 g, 83%); bp  $53-55^{\circ}\text{C}$  (250  $\mu\text{m}$ );  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$   $-124.3$  (s) (lit.<sup>9</sup>  $\delta$   $-125.1$ ).

**1,2-Bis(methylphosphino)benzene (6).** A solution of diphosphine **5** (2.04 g, 14.4 mmol) in THF was treated with a 5.01 M hexane solution of *n*-butyllithium (5.8 mL, 29.1 mmol) at  $-78^{\circ}\text{C}$ , and the solution was stirred for 0.5 h. Methyl iodide (4.10 g, 28.9 mmol) was then added at  $-78^{\circ}\text{C}$  and the solution was allowed to warm to room temperature. Water (10 mL) was added, the layers were separated, and the aqueous layer was extracted with ether ( $2 \times 30$  mL). The combined organic extracts were dried and concentrated, and the residue was distilled to give **6** as a colorless, air-sensitive liquid (2.0 g, 83%); bp  $69-70^{\circ}\text{C}$  (300  $\mu\text{m}$ );  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.4 (m, 4 H), 4.85 (dm,  $^2J_{\text{PH}} = 225$  Hz, 1 H), 4.4 (dm,  $^2J_{\text{PH}} = 216$ , 1 H), 1.47 (narrow m, 3 H), 1.39 (narrow m, 3 H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  143 (t,  $J = 5.6$  Hz), 133.1 (t,  $J = 5.0$  Hz), 5.9 (t,  $J = 3.7$  Hz);  $^{31}\text{P}$  NMR  $\delta$   $-75.7$  (s),  $-74.6$  (s) (ratio 1:1). Anal. Calcd for  $\text{C}_8\text{H}_{12}\text{P}_2$ : C, 56.48; H, 7.11. Found: C, 56.38; H, 7.17.

**1,2-Bis(dimethylphosphino)benzene (7).** A solution of **6** (5.4 g, 31.8 mmol) in ether (100 mL) was treated with a 3.3 M hexane solution of *n*-butyllithium (23 mL, 76 mmol) at room temperature. Methyl iodide (9.1 g, 64 mmol) in ether (25 mL) was added to this solution at room temperature, and the reaction mixture was stirred for 0.5 h. Water (50 mL) was added, the layers were separated, and the ether layer was dried and concentrated. Distillation of the residue gave **7** as a colorless liquid (5.5 g, 87%); bp  $139-141^{\circ}\text{C}$  (15 mm) (lit.<sup>1c</sup> bp  $92^{\circ}\text{C}$  (0.4-0.5 mm));  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$   $-55.3$  (s).

**1,2-Bis(2-propylphosphino)benzene (6b).** A solution of diphosphine **5** (1.72 g, 12.1 mmol) in THF (30 mL) was treated with a 1.90 M hexane solution of *n*-butyllithium (12.8 mL, 24.3 mmol) at  $-78^{\circ}\text{C}$ . The solution was warmed to and maintained at  $-50^{\circ}\text{C}$  as 2-bromopropane (3.0 g, 24.4 mmol) in THF (20 mL) at  $-25^{\circ}\text{C}$  was added (0.5 h). The resulting mixture was warmed to room temperature, stirred for 0.5 h, and then quenched with water (30 mL). The layers were separated, and the aqueous layer was extracted with ether ( $2 \times 50$  mL). The combined organic extracts were washed with water (50 mL), dried, and concentrated. The residue was distilled to give a colorless, air-sensitive liquid (2.04 g, 74%), bp  $71-83^{\circ}\text{C}$  (190  $\mu\text{m}$ ). The  $^{31}\text{P}$  NMR spectrum ( $\text{CDCl}_3$ ) exhibited peaks consistent with the monoalkylated di-

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(8) Fritzsche, H.; Hasseroth, V.; Korte, F. *Chem. Ber.* 1965, 98, 1681.

(9) Species **5** was prepared in unspecified yield by the  $\text{LiAlH}_4$  reduction of the tetraethoxy analogue of **3**. Issleib, K.; Liessring, E.; Meyer, H. *Tetrahedron Lett.* 1981, 22, 4475.

phosphine,  $\delta$  -29.7 (d,  $J$  = 67 Hz, PPh<sub>2</sub>-i) and -122.6 (d,  $J$  = 67 Hz, PH<sub>2</sub>), the trialkylated diphosphine  $\delta$  -1.7 [d,  $J$  = 108 Hz, P(Pr-*i*)<sub>2</sub>] and -23.6 (d,  $J$  = 108 Hz, PPh<sub>2</sub>-i), and **6b** (meso and *dl*),  $\delta$  -27.6 (s) and -31.5 (s); these species were present in an estimated ratio of 1:1:10, respectively. The mixture was redistilled to give three equal fractions (0.6 g) boiling over the range 120-130 °C (5 mm). The first fraction was enriched in the monoalkylated diphosphine and the third in the trialkylated material, and the second was further enriched in **6b** (estimated ratio mono:tri:6b = 1:1:20): <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  7.5 (m, 4 H), 4.2 (dm,  $J$  = 200 Hz, 2 H), 2.3 (m, 2 H), 1.2 (m, 12 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 140.6 (t,  $J$  = 5.3 Hz), 135.7 (t,  $J$  = 5.2 Hz), 128.2 (s), 24.3 (t,  $J$  = 2.8 Hz), 22.0 (t,  $J$  = 5.3 Hz). Anal. Calcd for C<sub>12</sub>H<sub>20</sub>P<sub>2</sub>: C, 63.71; H, 8.91. Found: C, 63.85; H, 8.86.

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tional Science Foundation (Grant CHE81-13090), the Robert A. Welch Foundation (Grant F573), and the Air Force Office of Scientific Research (Grant AFOSR-79-0090).

**Registry No.** **3**, 15104-46-8; **4**, 15104-43-5; **5**, 80510-04-9; *meso-6a*, 87532-91-0; *dl-6a*, 87532-95-4; *meso-6b*, 87532-92-1; *dl-6b*, 87532-94-3; **7**, 7237-07-2; trimethyl phosphite, 121-45-9; 1,2-dichlorobenzene, 95-50-1; methyl iodide, 74-88-4; 2-bromopropane, 75-26-3; 1-(di-2-propylphosphino)-2-(2-propylphosphino)benzene, 87532-93-2.

**Supplementary Material Available:** Additional experimental data (2 pages). Ordering information is given on any current masthead page.

## Communications

### Study of Group 8 Metal Promoters in the Cobalt-Catalyzed Carbonylation of Methanol to Acetaldehyde

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**Summary:** Transition-metal halides, MCl<sub>3</sub>·3H<sub>2</sub>O, where M = Rh, Ir, and Ru, have been found to be promoters for the cobalt-catalyzed carbonylation of methanol to acetaldehyde, and their role as promoters has been investigated. RhCl<sub>3</sub>·3H<sub>2</sub>O is known to stoichiometrically liberate HI when reacted in the presence of LiI and carbon monoxide. This liberated acid acts as a temporary promoter for the carbonylation as a result of rapid formation of methyl iodide from methanol and HI. The same temporary promotion is observed by substituting equimolar amounts of HI for RhCl<sub>3</sub>·3H<sub>2</sub>O. Under identical reaction conditions, the addition of IrCl<sub>3</sub>·3H<sub>2</sub>O or RuCl<sub>3</sub>·3H<sub>2</sub>O is shown to result in a similar type of promotion.

Multimetallic catalysts are of interest due to the potential for the different metals cooperating during chemical transformations.<sup>1</sup> It is hoped that this cooperativity will aid in the design of new, more selective catalysts that will provide high reaction rates and operate under mild conditions. Numerous claims and reports of the use of two or more metals to catalyze various reactions have appeared in the literature.<sup>2</sup> However, few homogeneous, mul-

timetallic catalysts have been substantiated.<sup>3</sup> We have been studying the cobalt/iodide catalyzed reductive carbonylation of methanol to acetaldehyde<sup>4</sup> and have found that the addition of group 8 metal salts as promoters results in an increase in the rate of reaction. We report here that this rate enhancement is not due to metal cooperativity, but it is a result of the ability of the promoting metal to generate acid in situ.

Group 8 metal salts such as RhCl<sub>3</sub>·3H<sub>2</sub>O, IrCl<sub>3</sub>·3H<sub>2</sub>O, and RuCl<sub>3</sub>·3H<sub>2</sub>O are effective to varying degrees as cocatalysts with Co(OAc)<sub>2</sub>·4H<sub>2</sub>O/LiI for the carbonylation of methanol to acetaldehyde (Table I).<sup>5</sup> The observation that all of the promoting metal salts are almost equally effective

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(3) The Wacker Process for the carbonylation of ethylene to acetaldehyde uses a palladium/copper bimetallic catalyst. There is strong evidence that the cobalt-catalyzed hydroformylation is bimetallic.<sup>2a</sup> The cobalt/iodide and various cobalt/ruthenium/iodide based catalysts for the carbonylation of methanol to acetaldehyde or ethanol are examples where bimetallic cobalt catalysis as in hydroformylation is observed. However, the role of ruthenium in the latter is only to catalyze the reduction of acetaldehyde to ethanol and does not interact in a cooperative manner with cobalt in any key reaction step.<sup>1b</sup>

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(5) The reactants are loaded into a 300-mL Hastelloy C autoclave designed to operate in a rocking mode. The autoclave is pressurized with 100 psig of 1/1 CO/H<sub>2</sub> at room temperature and vented. The autoclave is repressurized to 100 psig, sealed, heated, and rocked until the desired reaction temperature is reached. Then additional CO/H<sub>2</sub> gas mixture is added until the desired pressure is reached. The time at which the desired autoclave internal pressure is reached is taken as T<sub>0</sub>. Reactor pressure is maintained at the preset value during the experiment by adding the CO/H<sub>2</sub> gas mixture from a surge tank. When the predetermined reaction time is complete, the autoclave is rapidly cooled by a stream of cold air. After the gas is vented from the autoclave, the reaction product is analyzed by gas chromatographic methods with a POROPAK Q column with an acetonitrile internal standard.

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