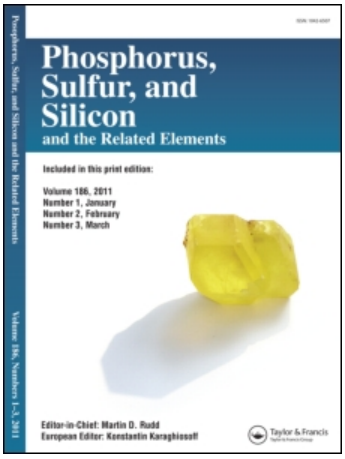

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THE REACTION OF DIBENZYLMERCURY WITH SECONDARY PHOSPHINES: PHOSPHORUS–PHOSPHORUS BOND FORMATION VERSUS BENZYL SUBSTITUTION

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In an attempt to find a simple, high yield synthetic method to create a phosphorus-phosphorus bond from phosphorus-hydrogen bonds, we have investigated the reaction of dibenzylmercury DBM with secondary phosphines. The overall reaction is: DBM + $R_2PH \rightarrow$ toluene + Hg + $R_2P - PR_2$. Thus reaction of diphenylphosphine with DBM produces the desired coupled product tetraphenyldiphosphine in 85–90% yield. In contrast, the reaction of DBM with 1,3-bis(phenylphosphino)propane Ph(H)P-$(CH_2)_3$-P(H)Ph produces the benzyl-substituted product Ph(Bz)P-$(CH_2)_3$-P(Bz)Ph rather than the expected cyclic compound 1,2-diphenyl-1,2-diphospholane PhP-$(CH_2)_3$-PPh. The dioxide or disulfide of Ph(H)P-$(CH_2)_3$-P(H)Ph undergoes no reaction with DBM. The bulky 2,4,6-tris(tert-butyl)phenylphosphine $ArPH_2$ with DBM yields diastereomers of the coupled disecondary diphosphine Ar(H)P-P(H)Ar. The reaction of DBM with diphenylchlorophosphine results in a high yield of tetraphenyldiphosphine, but with phenyldichlorophosphine produces the benzyl-substituted product phenylbenzylchlorophosphine.

Key words: 1,3-bis(phenylphosphino)propane; 1,2-diphenyl-1,2-diphospholane; 2,4,6-tris(tertbutyl)-phenylphosphine; benzylchlorophenylphosphine; dibenzylmercury; tetraphenyldiphosphine

INTRODUCTION

A number of dialkylmercury compounds have found application as effective reagents for coupling main-group hydrides to form new element-element bonds. Postniknova *et al.*,[1] successfully synthesized the cyclopolyphosphine $(PhP)_5$ in 70–80% yield from the reaction of DBM and phenylphosphine.

$$PhPH_2 + DBM \rightarrow (PhP)_5 + \text{toluene} + Hg \qquad (1)$$

Rheingold[2] extended the use of DBM as a convenient and general reagent for the formation of homoatomic catenates from primary alkyl phosphines, arsines, and stibines. For example, treatment of $MeEH_2$(E = P, As, or Sb) with DBM lead to quantitative production of the respective cyclic pentamers (or polymer, in the case of the stibine). In an attempt to find a convenient and high yield method to form phosphorus–phosphorus bonds from secondary phosphines, we have investigated the use of DBM as a coupling reagent.

RESULTS AND DISCUSSION

The reaction of stoichiometric quantities of diphenylphosphine Ph_2PH and DBM produced an 85–90% yield of the desired product tetraphenyldiphosphine, together with 10% of the substitution product Ph_2PBz. The reaction required 1 week at room temperature or 2 days at 60°C in either benzene or tetrahydrofuran solvent. An excess of DBM only slightly accelerated the reaction.

$$Ph_2PH + DBM \rightarrow Ph_2P—PPh_2 + Ph_2PBz + \text{toluene} + Hg + \text{dibenzyl} \quad (2)$$

The existence of the side-product dibenzyl was confirmed by GC/MS and NMR data. The phosphorus-containing by-product Ph_2PBz was observed by ^{31}P NMR spectroscopy ($\delta = -10.6$ ppm).

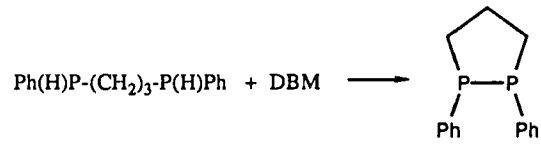
The reaction presumably proceeded through a free radical mechanism,[3] with DBM, when exposed to heat or light, forming the benzyl free radical. All of the products are consistent such a mechanism. Unlike DBM, dibenzyl did not act as a coupling reagent; once formed, it was unreactive. Thus in a separate experiment, a mixture of dibenzyl and Ph_2PH underwent no reaction at elevated temperature over 3 months.

While the yield of the desired coupled product $Ph_2P—PPh_2$ from Reaction (2) was quite high, the production of the by-product Ph_2PBz was surprising in comparison to Rheingold's quantitative reactions of primary phosphines, arsines and stibines with DBM (*vide supra*). Rheingold did observe substitution in addition to coupling in the reaction of dimethylarsine and DBM, where both tetramethyldiarsine and dimethylbenzylarsine were formed. Coupling, Reaction (3),[4,5] versus substitution, Reaction (4),[6] has also been observed in the reaction of triethyltin hydride with different organomercury compounds.

$$Et_3SnH + Et_2Hg \rightarrow Et_3Sn—SnEt_3 \quad (3)$$

$$Et_3SnH + Ph_2Hg \rightarrow Et_3SnPh \quad (4)$$

Using the reaction of Ph_2PH and DBM as a model reaction, we combined DBM with 1,3-bis(phenylphosphino)propane $Ph(H)P—(CH_2)_3—P(H)Ph$, hoping to obtain the cyclic diphosphine 1,2-diphenyl,1,2-diphospholane. However, the



(5)

reaction instead primarily produced the substitution product 1,3-bis(benzylphenylphosphino)propane with none of the expected coupling product 1,2-diphenyl,1,2-diphospholane.[7]

$$Ph(H)P—(CH_2)_3—P(H)Ph + DBM \rightarrow Ph(Bz)P—(CH_2)_3—P(Bz)Ph \quad (6)$$

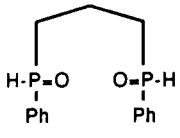
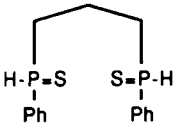
The $^{31}P[^1H]$ NMR spectrum in benzene solvent clearly showed two peaks with equal intensities at -18.6 ppm and -19.4 ppm, corresponding to the *d, l* and *meso* diastereomers of $Ph(Bz)P—(CH_2)_3—P(Bz)Ph$.[8] The ^{31}P NMR chemical shift

difference between the diastereomets was highly solvent dependent. For example, the difference was 0.1 ppm in tetrahydrofuran and 0.85 ppm in benzene. The ^{31}P NMR chemical shift is very similar to that of the structurally analogous $Ph_2P—(CH_2)_3—PPh_2$ at −17.3 ppm.[9] The formation of 1,3-bis(benzylphenylphosphino)propane was confirmed by its $^{13}C[^1H]$ NMR spectrum and the ^{13}C-^1H 2D spectrum. Three areas of carbon resonances in the methylene region were observed and assigned: 22.3 ppm (approximate triplet) for C(2), correlating to the proton resonance at 1.5 ppm; 28.5 ppm (approximate triplet) for C(1, 3), correlating to the proton resonances 1.8 ppm; and 36.3 ppm (doublet of doublets) for the methylene carbon on the benzyl group, correlating to the deshielded methylene protons on the benzyl group at 3.0 ppm. The relative intensities of the ^{13}C resonances were approximately 1:2:2, respectively. The ^{13}C DEPT spectrum further confirmed that all three carbon resonances correspond to methylene carbons. Doublet splitting of proton peaks arising from phosphorus coupling also validates the structural assignment.

Both the starting compound 1,3-bis(phenylphosphino)propane and 1,3-bis(benzylphenylphosphino)propane are air-sensitive. Upon contact with air or H_2O_2, the respective dioxides were produced; upon reaction with elemental sulfur, the respective disulfides were produced. The ^{31}P NMR and IR data for the dioxide and disulfide of 1,3-bis(phenylphosphino)propane are tabulated in Table I. The dioxide of 1,3-bis(benzylphenylphosphino)propane was a sticky white solid, very resistant to dissolution in common organic solvents. The ^{31}P NMR chemical shift was −43.7 ppm in acetone solvent. The disulfide of 1,3-bis(benzylphenylphosphino)propane[10] was slightly soluble in acetone, and upon recrystallization had a melting point of 180°C and a ^{31}P chemical shift was −46.9 ppm. The disulfide was also characterized by its mass spectrum. The

TABLE I

NMR and IR data for 1,3-bis(phenylphosphoryl)propane and 1,3-bis(phenylthiophosphoryl)propane

Compound	$\delta^{31}P[^1H]$[a]	$^1J_{PH}$	IR (ν, cm^{-1})[b]
	22.3 d	463.2	3430 s, 3040 w, 2926 s 2359 w, 1705 w, 1591 w, 1437 s, 1398 w, 1249 w, 1159 s, 1116 s, 1068 w, 979 m, 750 s, 694 s, 495 m
	26.5 d[c] 25.8 d[c]	476.9 472.3	3371 s, 3057 s, 2928 s, 2328 m, 1969 w, 1903 w, 1819 w, 1707 s 1587 m 1487 s, 1435 s, 1400 s 1363 s, 1311 m, 1222 m, 1180 s, 1149 s, 1116 s, 1026 m, 999 m, 956 s, 906 s, 802 m, 688 s, 632 s, 601 m, 507 s

[a]d = doublet. [b]s = strong, m = medium, w = weak. [c]Diasteriomers individually observable

dioxide and disulfide derivative of the parent 1,3-bis(phenylphosphino)propane are resistant to either coupling or substitution by DBM, with no reaction occurring even after one week at 80°C.

In an effort to examine the reactivity of DBM towards the P—H bond in a highly sterically hindered environment, we examined the reaction of DBM with tris(2,4,6-tert-butyl)phenylphosphine $ArPH_2$. It has been shown that this phosphine is so extremely sterically hindered that cyclization to $(ArP)_n$ is not possible; rather the stable ArP=PAr is formed.[11] We found that the reaction of DBM with $ArPH_2$ over 20 hours at ambient temperature in THF solvent produced a 70% yield of the diphosphine Ar(H)P—P(H)Ar,[12] as monitored by ^{31}P NMR spectroscopy. The compound Ar(H)P—P(H)Ar was identified by mass spectrometry and by comparison to an authentic sample. The $^{31}P[^1H]$ NMR spectrum exhibited two singlets at −63.9 and −63.1 ppm in a 6:1 ratio, respectively, corresponding to two diastereomers. The same ratio of isomers is obtained irrespective of the synthetic method. We assigned the predominate isomer to the *trans* form of the *meso* isomer, with the *d, l* enantiometric pair being the minor resonance.[8,13]

As an adjunct to the study, we examined the reaction of phenylchlorophosphines with DBM. The reaction of $PhPCl_2$ with DBM for 24 hours at 60°C yielded the simple monosubstituted product Ph(Bz)PCl [$\delta(^{31}P) = 88.2$ ppm] in quantitative yield, with no disubstituted product $PhP(Bz)_2$ or coupled products such as Ph(Bz)P—P(Bz)Ph. Similar behavior has been noted for $MeECl_2$(E = P, As, or Sb).[2] Substituting Ph_2PCl for $PhPCl_2$, the reaction with DBM for three days at ambient temperature lead to the coupled diphosphine $Ph_2P—PPh_2$ in high yield with only a trace of the substitution product Ph_2PBz.

Although electronic factors are undoubtedly important, it appears that steric factors generally determine the utility of DBM as a coupling reagent to form phosphorus–phosphorus bonds from phosphorus-hydrogen bonds. In the case of the reaction of 1,3-bis(phenylphosphino)propane with DBM, entropy factors probably also are important in the formation of the substitution product 1,3-bis(benzylphenylphosphino)propane rather than the coupled ring product 1,2-diphenyl,1,2-diphospholane.

EXPERIMENTAL

Most of the compounds and chemical procedures required rigorous exclusion of water and/or oxygen. Standard inert atmosphere and high vacuum line techniques were used.[14] All solvents were dried according to literature methods.[15] NMR measurements were recorded on an IBM AF-300 FT NMR spectrometer. All NMR data were reported relative to the following external standards: ^1H(TMS), ^{13}C(TMS), and ^{31}P(85% H_3PO_4), with positive values indicating downfield chemical shifts. Mass spectral data were obtained on a Hewlett-Packard 5995-B gas chromatography/mass spectrometer operating at an ionizing current of 70 ev.

General compound preparation and identification DBM was prepared by the method of Gilman and Brown,[16] followed by two recrystallization from chloroform. The purity was verified by proton NMR spectroscopy and melting point.[17] Diphenylphosphine was prepared by the $LiAlH_4$ reduction of diphenylchlorophosphine (Aldrich) in diethylether, and was purified by vacuum distillation.[18] Tetraphenyldiphosphine $Ph_2P—PPh_2$ was synthesized by the reaction of diphenylchlorophosphine and Mg.[18] The compound 1,3-bis(phenylphosphino)propane was obtained commercially (Strem) or by a modified synthesis of Issleib and Krech.[18] Tris(2,4,6-tert-butyl)phosphine was prepared and characterized according to literature methods.[12]

Reaction of phosphines with DBM The reaction of a phosphine and DBM was performed in an 5-mm NMR tube both with and without solvent. In a typical reaction, diphenylphosphine (0.372 g, 2.00 mmol) was mixed with DBM (0.762 g, 2.00 mmol) inside a Na/K-dried, inert-atmosphere box. The tube was evacuated and flame-sealed. The reaction proceeded for 10 days at either ambient temperature or at 60°C, and was constantly monitored by ^{31}P NMR spectroscopy. All other reactions of DMB with phosphines were performed in a similar manner.

Oxodation and sulfurination reactions of 1,3-bis(phenylphosphino)propane and of 1,3-bis(benzylphenylphosphino)propane Oxidations were performed by exposing a known amount of the phosphine to either air or H_2O_2. Sulfurinations were performed by mixing the neat phosphines under inert atmosphere with a slight excess of elemental sulfur, followed by recrystallization from acetone.

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