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PHOSPHINOMETHYLLITHIUM COMPOUNDS
IV. AN IMPROVED METHOD OF PREPARATION AND SOME SYNTHETIC APPLICATIONS

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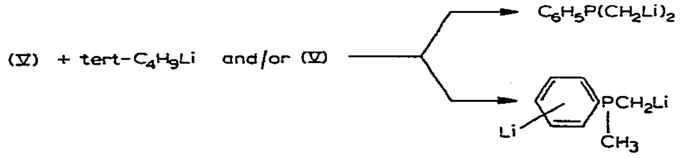
INTRODUCTION

In the prior papers of this series two methods for the preparation of some α-phosphinoalkyllithium compounds were described[1,2]. Thus, [diphenyl-(I), methylphenyl-(II), di-n-hexyl-(III), and dodecylmethyl-(IV)-phosphino] methyllithium were prepared by reacting the corresponding tertiary organophosphines with tert-butyllithium in hydrocarbon solvents[1]. (Diphenylphosphino)methyllithium was also obtained in low yield from the metalation of diphenylmethylphosphine with n-butyllithium in ether, a method that failed to give significant amounts of (II)–(IV)[1]. Tri-n-butylphosphine, a compound which on metalation would afford a secondary phosphinocarbanion, was essentially inert to reaction with either tert-butyllithium in hydrocarbon solvents or n-butyllithium in ether[1]. However, some other secondary phosphinoalkyllithium compounds were successfully prepared by additions of n- and tert-butyllithium to diphenyl- and di-n-butylvinylphosphines[2].

$$>PCH{=}CH_2 + RLi \rightarrow >\underset{\displaystyle Li}{PC}HCH_2R \quad R = n\text{-}C_4H_9,\ tert\text{-}C_4H_9 \qquad (1)$$

The relative rates of formation of the phosphinomethyllithium compounds from the earlier metalation studies varied considerably and in an unexpected manner. The optimum yields of (I), (II), and (III), as established by the classical carbonation technique, were 36% (312 h), 43% (48 h), and 45% (41 h), respectively[1]. Longer reaction times of tert-butyllithium with dimethylphenylphosphine or di-n-hexylmethylphosphine did not afford any significant increase in yields of (II) or (III).

$$C_6H_5P(CH_3)_2 + tert\text{-}C_4H_9Li \longrightarrow \underset{(V)}{C_6H_5(CH_3)PCH_2Li} + C_4H_{10} \qquad (2)$$



(3)

By employing more sophisticated methods of analysis, *i.e.*, ^{31}P NMR and mass spectral analyses, it was demonstrated that the preparations of (II) and (IV) were complicated by the formation of varying amounts (up to 38%) of dimetalated compounds[3]. To account for these products the following reaction scheme, using dimethylphenylphosphine as a model, was advanced. The initial step involves a selective methyl metalation (2) followed by a non-selective secondary dimetalation (3).

We now present a method for the preparation of these phosphinomethyllithium compounds which overcomes most of the difficulties inherent in the earlier method, *i.e.*, low and varying yields of the desired metalated methylphosphines, prolonged reaction times, complicating extensive formation of dimetalated phsophines, and the necessity for using the more hazardous tert-butyllithium as the metalating reagent.

PREPARATION OF PHOSPHINOMETHYLLITHIUM COMPOUNDS

It has been found that the 1 : 1 complex of n-butyllithium and tetramethylethylenediamine (TMEDA), described recently by Eberhardt and Butte[4], and Langer[5], for the teleomerization of ethylene, effects relatively rapid metalations of diphenylmethyl-, dimethylphenyl-, and dimethyldodecylphosphines at room temperature. For example, diphenylmethylphosphine was converted to (I) in 70% yield after only a two hour reaction time by a stoichiometric amount of the n-butyllithium/TMEDA complex. This finding contrasts quite dramatically with the 36% yield of (I) obtained from the metalation of the same methylphosphine with tert-butyllithium over a 312 hour period.

The rates of metalation of dimethylphenylphosphine and dimethyldodecylphosphine by the n-butyllithium/TMEDA complex were similarly rapid relative to the earlier method employing tert-butyllithium in hydrocarbon solvents. Thus, (II) and (IV) have been obtained in yields of 65% and 44%, respectively, during one and six hours of contact with the metalating complex.

The extent and relative rates of metalation of the three methylphosphines

TABLE 1

^{13}P NMR SPECTRAL ANALYSIS OF METALATED METHYLPHOSPHINES

Exp. No.	*Phosphine*[a]	*Time (h)*	*Chem. (ave.) shift of monometalated phosphine (ppm)*	*Monometalated phosphine (%)*	*Deuterium oxide quenched aliquots*[c]		
					d_0	d_1	d_2
1	Diphenylmethylphosphine	2.25	−2.6	70			
2[a]		1		84			
3	Dimethylphenylphosphine	1	+22.4	65			
4		4.5		75	28.1	67.6	4.3
5		7.5		70[b]	21	65	14
6	Dimethyldodecylphosphine	2.25	+35.2	44			
7		6		63			
8		24		80	22.9	75.3	1.8
9		41.5		87	18.6	78.2	3.2

[a] All reactions were run using a 1 : 1 : 1 stoichiometry of phosphine, TMEDA, and n-butyllithium, with the exception of Exp. 2 in which a 25% excess of the complex was employed. [b] An additional peak at +21 ppm corresponding to a dimetalated dimethylphenylphosphine[3] was also apparent. [c] Analyzed as the phosphine sulfides[3].

by the complex were established by ^{31}P NMR and mass spectral analyses. These data are summarized in Table 1.

A ^{31}P NMR spectral analysis of a diphenylmethylphosphine/n-butyllithium/TMEDA metalation mixture after one hour of contact exhibited three signals, at −2.6 ppm, +27.4 ppm, and +29 ppm, corresponding to (I) (70%), diphenylmethylphosphine[6] (27%), and an impurity (3%) present in the starting material. A similar analysis of the mixture resulting from a reaction of dimethylphenylphosphine with the complex during one hour revealed two distinct signals at +22.9 ppm and +45.5 ppm, corresponding to (II) (65%)[3] and starting phosphine[6] (35%). It was of particular interest to note that the signals at +21, +24.9, and +27.8 ppm, which represent dimetalated dimethylphenylphosphine[3], were barely observable, suggesting that these species were present in only trace amounts. This fact was subsequently confirmed by mass spectral analysis as discussed below.

A ^{31}P NMR spectral analysis of metalated dimethyldodecylphosphine (after 24 h) demonstrated the predominance of (IV) (80%) at +35.2 ppm and some (20%) starting phosphine at +52.7 ppm. No other signals were evident in the spectrum.

The ^{31}P NMR spectral analysis of these three metalation mixtures suggested that dimetalation was occurring to only a minor extent in metalations with the n-butyllithium/TMEDA complex at these relatively short reaction times. To confirm this interesting observation, aliquots from the metalations of dimethyl(phenyl or -dodecyl-)phosphine were quenched with deuterium oxide and analyzed by mass spectroscopy. As is evident from the data in Table 1, only minor amounts of phosphine-d_2 were obtained at reaction times when dimethylphenylphosphine and dimethyldodecylphosphine had been converted to 68% (II) and 75% (IV), respectively*. These findings are quite significant, since this information, in conjunction with the finding that the complex effects rapid metalations of the methylphosphines, demonstrates that this new system affords a valuable method for the preparation of phosphinomethyllithium compounds. However, as the data in Table 1 indicate, the favorable high ratio of mono- to dimetalated species can be quite time dependent. Thus, by simply extending the metalation time of dimethylphenylphosphine from 4.5 to 7 hours, the ratio of mono- to dimetalation changes from 16/1 to 4.7/1. The time factor is far less significant in the metalation of dimethyldodecylphosphine (see Table 1).

Surprisingly, tri-n-butylphosphine was found to be quite inert to the metalating complex over a 28 h period, as evidenced by ^{31}P NMR spectral analysis.

It is apparent from the data in Table 1 that the order of reactivity of the three methylphosphines toward the complex is $(C_6H_5)_2PCH_3 \cong C_6H_5P(CH_3)_2 > C_{12}H_{25}$-$P(CH_3)_2$. This would appear to be the order of reactivity expected from a consideration of electronic facors, since it is logical to assume that phenyl groups would increase the effective electronegativity of a phosphino group relative to the alkyl groups, and, as a consequence, enhance the removal of a proton from a methylphosphine. Presumably, the inductive effect of the phenyl groups would also contract the relatively diffuse *d*-orbitals of phosphorus[7], which would result in a more favorable overlap of the phosphorus orbitals with the adjacent carbanion.

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* It was previously[3] shown that phosphine-d_1 and -d_2 result from the quenching of mono- and dimetalated phosphines, respectively.

This order of reactivity contrasts with that reported[1] earlier for the metalations of the methylphosphines with tert-butyllithium. It is now suggested that the relative decreased reactivity of diphenylmethylphosphine to metalation by tert-butyllithium[1] is due to steric factors, and that the reactivity series established with the n-butyllithium/TMEDA complex as the metalating agent more accurately reflects the electronic factors involved in the metalation of methylphosphines.

This information then, in conjunction with the earlier findings[1] that methylphenylphosphines undergo a selective initial methyl metalation[1,3], that dimethyldodecylphosphine is metalated *ca.* 15 times more rapidly than the corresponding amine[1], that vinylphosphines undergo Michael addition reactions with organolithium compounds[2], and that tri-n-butylphosphine is relatively inert to metalation[1], suggests the following generalizations. (1) *d*-Orbital resonance appears to constitute some of the driving force for the metalations of the methylphosphines and the Michael additions of n-butyllithium to the vinylphosphines; (2) electron withdrawing groups on the trivalent phosphorus atom enhance the rates of metalation of methylphosphines; and (3) the metalation reactions are controlled by delicate energy factors, such as the replacement of a hydrogen by an alkyl group on the carbon atom that undergoes metalation*.

The metalation mixtures obtained from reactions of the n-butyllithium/TMEDA complex with two of the methylphosphines were further characterized by carbonation and subsequent oxidation or sulfurization. The (I) and (IV) afforded 44 and 45% yields (pure) of (carboxymethyl)diphenylphosphine sulfide[8], and (carboxymethyl)dodecylmethylphosphine oxide, respectively. From both experiments, the yield of recovered starting phosphine approximated that expected from a consideration of the data in Table 1.

The structure assignment of (carboxymethyl)dodecylmethylphosphine oxide, $C_{12}H_{25}(CH_3)P(O)CH_2CO_2H$, was confirmed by NMR spectral analysis (see Table 2) and an alternate synthesis of the compound by an established procedure[9], involving the metalation of dimethyldodecylphosphine oxide and subsequent carbonation.

Compound (I) was further characterized by ^1H NMR spectral analysis of the product resulting from quenching with D_2O. As expected, the $>PCH_2D$ (as the sulfide) portion of the spectrum exhibited a six line pattern (two of the six lines being masked by the doublet arising from undeuterated phosphine sulfide); $J(P{-}H) = 12.8$ cps, and $J(H{-}D) = 1.9$ cps[12]. The amount of monodeuterophosphine, as estimated by integration, was *ca.* 75%, which was in accord with a ^{31}P NMR spectral analysis of a similar sample.

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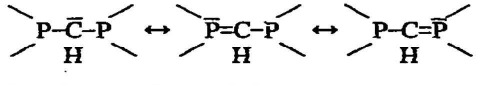
* The substitution of a phosphino group for a hydrogen atom, however, greatly accelerates the rate of metalation. In contrast to diphenylmethylphosphine, bis(diphenylphosphino)methane undergoes a very rapid (complete in less than 0.1 h) metalation when treated with either n-butyllithium or phenyllithium in ether. This finding is reasonable, since the second phosphino group is expected to enhance the acidity of the methylene protons owing to the added resonance stabilization:



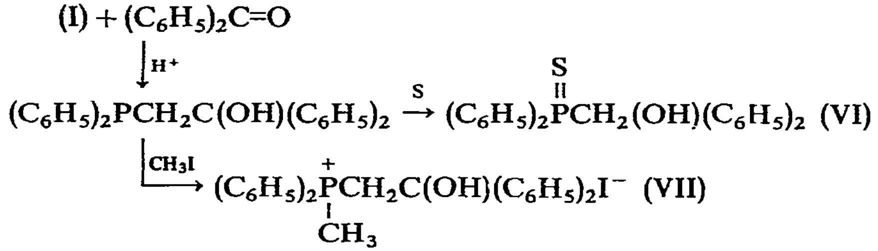
Unpublished results from this laboratory.

SOME REACTIONS OF (DIPHENYLPHOSPHINO)METHYLLITHIUM

To demonstrate the utility of phosphinomethyllithium compounds as intermediates in the synthesis of carbon-functionally substituted phosphines, (I) was chosen as a model for study, and was reacted with chlorodiphenylphosphine and phenoxydiphenylphosphine to give the known[10] bis(diphenylphosphino)methane.

$$I + XP(C_6H_5)_2 \rightarrow (C_6H_5)_2PCH_2P(C_6H_5)_2 \ (41\text{–}51\%) \quad X = Cl, C_6H_5O.$$

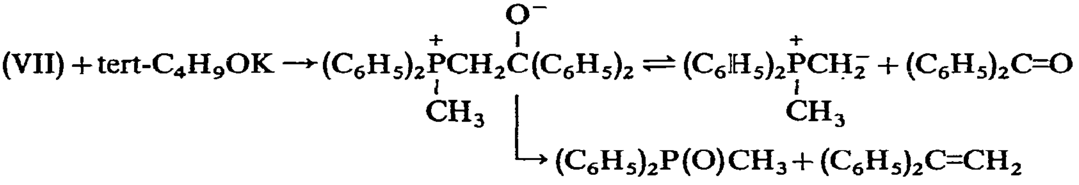
Also, (I) was reacted with benzophenone to give, subsequent to treatments with sulfur and methyl idodide, (2,2-diphenyl-2-hydroxyethyl)diphenylphosphine sulfide (VI) and (2,2-diphenyl-2-hydroxyethyl)diphenylmethylphosphonium iodide (VII) in 56 and 75% yields, respectively.



$$\begin{array}{l} (I) + (C_6H_5)_2C{=}O \\ \downarrow H^+ \\ (C_6H_5)_2PCH_2C(OH)(C_6H_5)_2 \xrightarrow{S} (C_6H_5)_2\overset{S}{\overset{\|}{P}}CH_2(OH)(C_6H_5)_2 \ \text{(VI)} \\ \xrightarrow{CH_3I} (C_6H_5)_2\overset{+}{\underset{CH_3}{P}}CH_2C(OH)(C_6H_5)_2I^- \ \text{(VII)} \end{array}$$

The phosphine sulfide was identified by ^{31}P and ^{1}H NMR spectral analyses and peroxide oxidation to the corresponding (known)[9] phosphine oxide (see Table 2 for NMR data).

The structure assignment of the phosphonium salt was confirmed by degradation with base. Thus, as expected from a published report[11], the betaine intermediate



$$\text{(VII)} + tert\text{-}C_4H_9OK \rightarrow (C_6H_5)_2\overset{+}{\underset{CH_3}{P}}CH_2\overset{O^-}{C}(C_6H_5)_2 \rightleftharpoons (C_6H_5)_2\overset{+}{\underset{CH_3}{P}}CH_2^- + (C_6H_5)_2C{=}O$$
$$\rightarrow (C_6H_5)_2P(O)CH_3 + (C_6H_5)_2C{=}CH_2$$

underwent two modes of decomposition to give a phosphorus ylid, benzophenone, diphenylmethylphosphine oxide, and 1,1-diphenylethylene. From a typical run, subsequent to five hours reaction time, benzophenone (37%) and 1,1-diphenylethylene (35%) were isolated.

EXPERIMENTAL

All reactions and manipulations involving phosphines and organolithium compounds were performed under an atmosphere of oxygen-free argon. The n-butyllithium used in this study was obtained from a commercial source. NMR spectra were obtained on Varian Associates HR-60 (phosphorus) and HA-100 (proton) spectrometers.

(1) *Typical preparation of a phosphinomethyllithium compound*

To a 50 ml round-bottom flask equipped with magnetic stirrer and argon inlet adapter there was added successively, 13.3 ml of 1.5 molar (0.02 mole) n-butyllithium in hexane, 2.32 g (0.02 mole) of TMEDA, and 0.02 mole of the methylphosphine. In the metalations of diphenylmethylphosphine and dimethylphenylphosphine, yellow precipitates were observed after *ca.* 0.25 h and 1 h, respectively. Subsequent to stirring for the desired length of time at room temperature, sufficient tetrahydrofuran was added to dissolve the insoluble material so that the metalated phsophines could be readily handled by syringe techniques.

(2) *Reaction of (diphenylphosphino)methyllithium with phenoxydiphenylphosphine*

A solution of (diphenylphosphino)methyllithium, prepared from 16.4 ml of 1.4 molar (0.023 mole) n-butyllithium in hexane, 2.7 g (0.023 mole) of TMEDA, 4 g (0.02 mole) of methyldiphenylphosphine, and 20 ml of tetrahydrofuran, was added dropwise to a solution of 8.4 g (0.03 mole) of phenoxydiphenylphosphine in 20 ml of tetrahydrofuran over 0.5 h. Subsequent to allowing the initially mildly exothermic reaction to stir for 2 h, 3 ml of the reaction mixture was drawn off and analyzed by ^{31}P NMR spectral analysis. Four signals were apparent in the spectrum, at -111 ppm ($PhOPPh_2$), $+5.8$ ppm (unknown), $+22.2$ ppm [$(Ph_2P)_2CH_2$], and $+27.2$ ppm (Ph_2PCH_3) in the ratio of *ca.* 1 : 1 : 5 : 1, respectively.

After an additional 3.5 h, the reaction mixture was added, under argon, to 1 l of rapidly stirred water. Filtration afforded 3.53 g (46%) of bis(diphenylphosphino)-methane, m.p. 111–114°. A crystallization from ethanol raised the melting point to 117.5–119.5°. An admixed melting point determination with an authentic sample[11] was not depressed.

The filtrate was thoroughly extracted with ether, concentrated, and treated with elemental sulfur. The resulting oil was dissolved in ether and hexane was added to incipient cloudiness. On standing, 0.58 g of material melting over a wide range crystallized. The material was boiled in carbon tetrachloride and filtered to give 0.28 g of insoluble compound, m.p. 251–256°. A ^1H NMR spectrum of the material exhibited a complex multiplet at τ 2.1–3.

The mother liquor of the above fraction was concentrated and subsequently dissolved in a mixture of $CHCl_3$ and ethanol. On prolonged standing, 0.48 g (5.3%) of crude bis(diphenylthiophosphinyl)methane, m.p. *ca.* 170°, crystallized. An infrared spectrum of the material was superimposable on that of an authentic sample (m.p. 183–185°) which was prepared from bis(diphenylphosphino)methane and an excess of sulfur. (Found: C, 66.7; H, 4.8. $C_{25}H_{22}P_2S_2$ calcd.: C, 66.96; H, 4.93%.) The compound exhibited a ^{31}P NMR signal at -34.5 ppm in chloroform and ^1H NMR signals centered at τ 2.45 (aromatic) and 6.01 (methylene, triplet, $J = 13$ cps) in deuterochloroform.

(3) *Reaction of (diphenylphosphino)methyllithium with benzophenone followed by treatment with methyl iodide*

A solution of (diphenylphosphino)methyllithium, prepared from 16.4 ml of 1.5 molar (0.023 mole) n-butyllithium, 2.9 g (0.025 mole) of TMEDA, 4 g (0.02 mole) of diphenylmethylphosphine, and 15 ml of tetrahydrofuran over 4.5 h, was added dropwise (0.5 h) to 4 g (0.022 mole) of benzophenone dissolved in 20 ml of tetrahydrofuran at 0°. During the addition a green color persisted but disappeared with time.

After 5 h, dilute aqueous ammonium chloride (1.3 g in 50 ml) was added to the chilled reaction mixture. The organic layer was separated and treated with 10.3 g (0.07 mole) of methyl iodide which resulted in an exothermic reaction and the formation of an insoluble oil. The addition of acetone caused the oil to dissolve with the formation of a small amount of solid. The solid, 1.2 g, m.p. 266–274° (dec.) was removed by filtration and identified as $(CH_3)_3N^+CH_2CH_2N^+(CH_3)_3\ 2I^-$.

The mother liquor was concentrated, leaving a gummy residue. On vigorous shaking with ether, 11.8 g (75%) of crude phosphonium salt crystallized, melting over the range of 88–95°. An analytical sample was prepared by dissolving a portion of the compound in chloroform and carefully adding ether to incipient cloudiness. On prolonged standing, the phosphonium salt crystallized, m.p. 200–203° (dec.). (Found: C, 61.6; H, 5.4; I, 24.5. $C_{27}H_{28}OPI$ calcd.: C, 61.8; H, 5.0; I, 24.2%.) The ^{31}P and ^{1}H NMR spectra confirmed the structure assignment (see Table 2).

TABLE 2

PROTON AND PHOSPHORUS NMR DATA OF DERIVATIVES

Phosphine derivative[a]	*^{31}P NMR chemical shift (ppm)*	*^{1}H NMR*[c,d,e]			
		Aromatic H	*PCH_3*	*PCH_2–*	*–OH(OCH_3)*
$(C_6H_5)_2P(S)CH_2C(OH)(C_6H_5)_2$	−34.6	2.65 (m)		6.42 (d) $J = 10.2$	3.42 (s)
$(C_6H_5)_2P(O)CH_2C(OH)(C_6H_5)_2$	−33.1	2.7 (m)		6.65 (d) $J = 9.6$	4.5 (m)
$(C_6H_5)_2(CH_3)\overset{+}{P}CH_2C(OH)(C_6H_5)_2I^-$	−20.7	2.6 (m)	7.18 (d) $J = 14.8$	5.51 (d) $J = 13.2$	4.46 (m)
$C_{12}H_{25}(CH_3)P(O)CH_2CO_2H$	−48.7		8.37 (d) $J = 12.8$	7.01 (d) $J = 14.8$	6.25 (s)

[a] All ^{31}P NMR spectra were obtained on $CHCl_3$ solutions of the compounds. A spinning 9 mm tube was employed. [b] Relative to 85% H_3PO_4. [c] Data recorded: chemical shift is in τ units (relative to tetramethylsilane), splitting pattern (s = singlet, d = doublet, m = multiplet), and coupling constant J (cps). [d] All ^{1}H NMR spectra obtained on $CDCl_3$ solutions of the compounds. [e] Integrations of the relative number of protons were in accord with the structure assignments.

(4) *Reaction of (diphenylphosphino)methyllithium with benzophenone followed by treatment with sulfur*

A solution of (diphenylphosphino)methyllithium, prepared from 32 ml of 1.4 molar (0.045 mole) n-butyllithium, 5.22 g (0.045 mole) of TMEDA, 6 g (0.03 mole) of diphenylmethylphosphine over 1.25 h, and 20 ml of tetrahydrofuran was added to 6.7 g (0.05 mole) of benzophenone dissolved in 17 ml of tetrahydrofuran at *ca.* −80° (required 1 h). The green colored reaction mixture was maintained at −80° for an additional hour, allowed to warm to −10° over 0.5 h, and was then treated with a dilute aq. solution (2.5 g in 50 ml) of ammonium chloride. The organic layer was removed and reacted with an excess of sulfur. The oil which was obtained on work-up was triturated with ether to give 4.55 g of (2-hydroxy-2,2-diphenylethyl)diphenylphosphine sulfide, m.p. 141–145°. Concentration afforded an additional 1.15 g of compound, m.p. 130–134°.

The mother liquor was chromatographed on alumina. Elution with hexane gave 0.19 g of material, m.p. 174–175°, ^{31}P NMR signal at -45.6 ppm, and ^1H NMR signals only in the region of τ 2.4–2.8. Continued elution with chloroform afforded a mixture of benzophenone and the β-hydroxyphosphine sulfide. Trituration with ether resulted in two crops of the phosphine sulfide; 1.05 g, m.p. 144–147°, and 0.19 g, m.p. 130–135°.

Continued elution with benzene gave a glassy-polymeric substance that was not further worked up.

The combined phosphine sulfide, 6.94 g (56%), was crystallized from a benzene/hexane mixture to give 4.71 g of compound, m.p. 148–150°. (Found: C, 75.3; H, 5.9; P, 7.34; S, 7.85. $C_{25}H_{23}OPS$ calcd.: C, 75.38; H, 5.55; P, 7.47; S, 7.74%.) See Table 2 for NMR data. A second crop of 0.63 g of less pure phosphine sulfide, m.p. 138–147°, was obtained on concentration of the mother liquor.

(5) *Base induced decomposition of (2-hydroxy-2,2-diphenylethyl)diphenylmethylphosphonium iodide*

To 5.24 g (0.01 mole) of crude phosphonium salt there was added 25 ml of 1,2-dimethoxyethane and 2.2 g (*ca.* 0.01 mole) of potassium tert-butoxide/tert-butanol which resulted in an immediate reaction as evidenced by the liberation of heat. The reaction mixture was then heated at 55° under argon for 3 h, cooled, and poured into water. The organic layer was separated and concentrated to give an oil.

The oil was carefully chromatographed on alumina to give the following fractions: (1) Hexane eluted 0.67 g (37%) of 1,1-diphenylethylene. An infrared spectrum of the olefin was superimposable on that of an authentic sample. Also, the GLC retention time of the compound was identical to that of authentic 1,1-diphenylethylene; (2) benzene eluted no detectable compounds; (3) ether as eluent produced 0.64 g (35%) of benzophenone which was identified by infrared spectral analysis and GLC retention time; and (4) ethanol eluted some crude diphenylmethylphosphine oxide, m.p. 96–105°. Attempts to purify the compound failed. A ^1H NMR spectrum confirmed the structure assignment: a doublet centered at τ 8.03 ($J = 12$ cps) and a multiplet centered at τ 2.35 owing to the methyl and aromatic protons in the correct area ratios.

(6) *Reaction of (diphenylphosphino)methyllithium with chlorodiphenylphosphine*

A solution of (diphenylphosphino)methyllithium, prepared from 14.3 ml of 1.6 molar (0.022 mole) n-butyllithium, 2.55 g (0.022 mole) of TMEDA, 4 g (0.02 mole) of diphenylmethylphosphine, and 10 ml of tetrahydrofuran over 2 h, was added dropwise to 4.75 g (0.022 mole) of chlorodiphenylphosphine dissolved in 15 ml of tetrahydrofuran. An immediate reaction occurred as evidenced by the liberation of heat and discharge of the brownish-yellow color of the phosphinomethyllithium compound. Subsequent to 1.5 h of stirring at room temperature, the reaction mixture was added to 500 ml of water with vigorous stirring. The insoluble material, 3.1 g (41%) of bis(diphenylphosphino)methane, m.p. 112–117°, was removed by filtration. A crystallization from a benzene/acetone mixture afforded 2.9 g of phosphine, m.p. 119–121°. An admixed melting point determination with an authentic sample[10] was not depressed. The filtrate was not further worked up.

(7) *Preparation of (carboxymethyl)dodecylmethylphosphine oxide*

To a mixture of 29.5 g (0.12 mole) of dimethyldodecylphosphine oxide[13] and 50 ml of ether there was added dropwise 75 ml of 1.6 molar n-butyllithium in hexane. An immediate reaction occurred as evidenced by the liberation of heat and the initial dissolution of the solid. Toward the end of the butyllithium addition, a copious quantity of semi-solid formed and made stirring difficult. To the reaction mixture, 35 ml of 1,2-dimethoxyethane was added, resulting in the dissolution of the insoluble material. The reaction mixture was then carbonated by the standard technique[1]. On work-up, 17.9 g (50%) of (carboxymethyl)dodecylmethylphosphine oxide, m.p. 83–85°, was obtained. (Found: C, 62.3; H, 10.9; P, 10.7. $C_{15}H_{31}O_3P$ calcd.: C, 62.1; H, 10.7; P, 10.7%.)

The methyl ester of the acid, (carbomethoxymethyl)dodecylmethylphosphine oxide, was prepared by a standard procedure which employed 5.8 g (0.02 mole) of acid, 30 ml of methanol, and 2 drops of conc. H_2SO_4 over 17 h at reflux. On work-up, 4.05 g (70%) of crude ester was obtained. Crystallizations from hexane afforded the analytical sample, m.p. 59–60°. The ^1H NMR spectrum of this compound was the same as that obtained for the acid (see Table 2) with two exceptions: (1) methoxy protons at τ 6.25 in place of acid proton, and (2) the $P-CH_3$ doublet was shifted to τ 8.4.

(8) *Carbonation of (dodecylmethylphosphino)methyllithium*

A solution of (dodecylmethylphosphino)methyllithium, prepared from 18 ml of 1.43 molar (0.026 mole) n-butyllithium in hexane, 2.8 g (0.024 mole) of TMEDA, and 5.55 g (0.024 mole) of dimethyldodecylphosphine, was carbonated by the technique previously described[1]. The resulting carboxylate was then oxidized with an excess of 10% hydrogen peroxide. Subsequent to destroying the excess peroxide with sodium sulfite, the organic layer was separated, dried over sodium sulfate, and concentrated to give 0.98 g (16.5%) of dimethyldodecylphosphine oxide, m.p. 79–82°. An infrared spectrum of the compound was superimposable on that of an authentic sample[13].

The aqueous layer was acidified and thoroughly extracted with ether and chloroform. Subsequent to drying over sodium sulfate, the combined extracts were concentrated to give 4.15 g (60%) of crude (carboxymethyl)dodecylmethylphosphine oxide, m.p. 73–78°. Crystallizations from benzene/hexane solvent combinations afforded 3.25 g of compound, m.p. 84–86°. The mother liquor was subjected to a vacuum of 0.55 mm at 95° to remove residual valeric acid. An NMR spectrum showed that the residue (0.45 g) contained *ca.* 0.2 g of acid and 0.25 g of dimethyldodecylphosphine oxide.

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SUMMARY

Three methylphosphines have been found to undergo rapid reactions with a

1:1 complex of n-butyllithium and tetramethylethylenediamine to give moderate to high yields of phosphinomethyllithium compounds. This method of preparation enjoys several advantages over the known method. The utility of phosphinomethyllithium compounds as intermediates in the synthesis of carbon-functionally substituted organophosphines has been demonstrated by the conversion of (diphenylphosphino)-methyllithium to $[(C_6H_5)_2P]_2CH_2$, $(C_6H_5)_2P(S)CH_2CO_2H$, $(C_6H_5)_2P(S)CH_2D$, $(C_6H_5)_2P(S)CH_2C(OH)(C_6H_5)_2$, and $(C_6H_5)_2(CH_3)P^+CH_2C(OH)(C_6H_5)_2I^-$.

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