STUDIES IN PHOSPHINEMETHYLENE CHEMISTRY

XIII*. ROUTES TO TRIPHENYLPHOSPHINE-HALOMETHYLENES AND -DIHALOMETHYLENES

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As part of a broad investigation of the action of organolithium reagents on quaternary phosphonium halides, we previously studied the action of phenyllithium on (chloromethyl)triphenylphosphonium bromide[5].

$$[(C_6H_5)_3PCH_2Cl]Br + C_6H_5Li \longrightarrow (C_6H_5)_3\overset{+}{P}-\overset{-}{C}HCl + C_6H_6 + LiBr \qquad (1)$$

This reaction, followed by reaction of the resulting triphenylphosphinechloromethylene with an aldehyde or ketone, led to a general vinylic chloride synthesis. It was of interest to see if a similar route to vinylic bromides and iodides could be developed. Accordingly, the action of phenyllithium on bromomethyl- and iodomethyltriphenylphosphonium halides was investigated.

When phenyllithium was added at room temperature to an equimolar quantity of (bromomethyl)triphenylphosphonium bromide suspended in diethyl ether, a red-orange color developed immediately and the phosphonium salt went into solution. Addition of an excess of cyclohexanone resulted in almost complete discharge of color. Gas chromatographic analysis of the volatile components showed the presence of benzene (53%), bromobenzene (46%), methylenecyclohexane (43%) and (bromomethylene)cyclohexane (46%). The attack of phenyllithium on the bromomethylphosphonium salt thus may be summarized as follows:

$$[(C_6H_5)_3PCH_2Br]Br \xrightarrow{C_6H_5Li} \begin{cases} \longrightarrow (C_6H_5)_3\overset{+}{P}-\overset{-}{C}HBr + C_6H_6 + LiBr \\ \longrightarrow (C_6H_5)_3\overset{+}{P}-\overset{-}{C}H_2 + C_6H_5Br + LiBr \end{cases}$$

A similar situation was encountered when phenyllithium was allowed to react with (iodomethyl)triphenylphosphonium iodide and the resulting brownish-orange solution was treated with cyclohexanone:

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* For Part XII see ref. 1; preliminary communications: refs. 2 and 3. Also Part IV of the series, "Halomethyl-Metal Compounds"; for Part III see ref. 4.

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$$[(C_6H_5)_3PCH_2I]I \xrightarrow{C_6H_5Li} \begin{cases} \longrightarrow (C_6H_5)_3\overset{+}{P}\text{-}\overline{C}HI + C_6H_6 + LiI \\ \longrightarrow (C_6H_5)_3\overset{+}{P}\text{-}\overline{C}H_2 + C_6H_5I + LiI \end{cases}$$

Benzene and iodobenzene were obtained in yields of 26 and 73 %, methylenecyclohexane and (iodomethylene)cyclohexane in yields of 55 and 22 % respectively.

Thus, in contrast to (chloromethyl)triphenylphosphonium bromide, the bromomethyl- and iodomethylphosphonium halides experience (formal) halogen cation abstraction as well as proton abstraction by the phenyllithium, and the former mode of attack is greatly favored in the case of (iodomethyl)triphenylphosphonium iodide. These results are not especially surprising; they are in line with the known relative reactivities of carbon–halogen linkages toward organolithium reagents[6]: C–Cl < C–Br < C–I. The results obtained find an interesting parallel in the reactions of *n*-butyllithium with the 1-halo-2,2-diphenylethylenes[7]:

$$(C_6H_5)_2C{=}CHCl \xrightarrow{C_4H_9Li} (C_6H_5)_2C{=}C(Cl)Li \longrightarrow C_6H_5C{\equiv}CC_6H_5 + LiCl$$

$$(C_6H_5)_2C{=}CHBr \xrightarrow{C_4H_9Li} \begin{cases} \longrightarrow (C_6H_5)_2C{=}C(Br)Li \longrightarrow C_6H_5C{\equiv}CC_6H_5 + LiBr & (57\,\%) \\ \longrightarrow (C_6H_5)_2C{=}CHLi & (34\,\%) \end{cases}$$

$$(C_6H_5)_2C{=}CHI \xrightarrow{C_4H_9Li} (C_6H_5)_2C{=}CHLi$$

Only lithium–hydrogen exchange was observed in the case of the chloro derivative; both lithium–hydrogen and lithium–halogen exchange with the bromide and solely lithium–halogen exchange in the case of the iodoethylene.

It would, of course, be desirable to have available a Wittig reaction procedure for vinylic bromides and iodides in which halogen-free olefins were not formed as well. Such a synthesis was reported by Köbrich[8] shortly after the initial publication of our results. It was claimed that the action of lithium piperidide on (bromomethyl)triphenylphosphonium bromide resulted in exclusive formation of triphenylphosphine-bromomethylene. However, only two examples[8,9] have been provided thus far, and the details of this work have not yet been published.

Our work with phenyl(dihalomethyl)mercury compounds[10] has led us to another specific, Wittig-reaction-based route to vinylic chlorides and bromides. The reaction of triphenylphosphine with carbenes and "carbenoid" reagents had been shown by several groups in 1960 to give phosphinemethylene reagents: $(C_6H_5)_3\overset{+}{P}\text{-}\overline{C}Cl_2$[11,12], $(C_6H_5)_3\overset{+}{P}\text{-}\overline{C}Br_2$[5,11,12], $(C_6H_5)_3\overset{+}{P}\text{-}\overline{C}HCl$[5,12]. Later investigators developed "one-pot" 1,1-dihaloolefin syntheses based on such reactions[14–16], *e.g.*:

$$2\,(C_6H_5)_3P + CCl_4 + 2\,RCHO \longrightarrow 2\,(C_6H_5)_3PO + RCH{=}CCl_2 + RCHCl_2 \qquad \text{(ref. 14)}$$

$$ClF_2COONa + (C_6H_5)_3P + RCHO \longrightarrow (C_6H_5)_3PO + RCH{=}CF_2 + NaCl + CO_2 \qquad \text{(ref. 16)}$$

The ready α-elimination of phenylmercuric bromide from $C_6H_5HgCX_2Br$ compounds[17] at 80° suggested that these mercurials might serve well in the preparation of 1,1-dihaloolefins in similar reactions with triphenylphosphine in the presence of aldehydes and ketones. This was found to be the case.

Initial experiments showed that a "one-pot" reaction of phenyl(bromodichloromethyl)mercury, triphenylphosphine and benzaldehyde occurred with facility in benzene solution at 80°, giving $C_6H_5CH{=}CCl_2$ in about 65–70 % yield:

$$C_6H_5HgCCl_2Br + (C_6H_5)_3PO + C_6H_5CH{=}O \longrightarrow C_6H_5HgBr + (C_6H_5)_3PO + C_6H_5CH{=}CCl_2$$

Such a reaction also was found to occur with cyclohexanone [to give (dichloromethylene)cyclohexane in 65 % yield] only when the refluxing benzene medium was replaced by refluxing *o*-xylene. Further experiments showed that such reactions occurred also with $C_6H_5HgCBr_3$, $C_6H_5HgCHClBr$ and $C_6H_5HgCHBr_2$, giving $RR'C{=}CBr_2$, $RR'C{=}CHCl$ and $RR'C{=}CHBr$ respectively. Of special interest is this new, apparently generally applicable synthesis of vinyl bromides in which yields averaged 52–55 %. The results of this work are summarized in Table 1. This mercurial-based procedure may have advantage over the preparation of $RR'C{=}CX_2$ via carbon tetrachloride and tetrabromide in many cases, since $(C_6H_5)_3PX_2$ is not formed in amounts equivalent

TABLE 1

PRODUCTS OF THE PHENYL(HALOMETHYL)MERCURIAL-BASED WITTIG REACTION

Mercurial	*Carbonyl compound*	*Haloölefin produced*	(% *yield*)	n_D^{25}	C_6H_5HgBr (%)	$(C_6H_5)_3PO$ (%)
$C_6H_5HgCHClBr$	*n*-Heptaldehyde	$CH_3(CH_2)_5CH{=}CHCl$	(82)	1.4380	91	79
	Benzaldehyde	$C_6H_5CH{=}CHCl$	(73)	1.5753[a]	84	71
	Cyclohexanone	cyclo-$C_6H_{10}{=}CHCl$	(77)		93	64
$C_6H_5HgCHBr_2$	*n*-Heptaldehyde	$CH_3(CH_2)_5CH{=}CHBr$	(53)	1.4598[b]	84	52
	Benzaldehyde	$C_6H_5CH{=}CHBr$	(55)	1.6056[c]	89	55
	Cyclohexanone	cyclo-$C_6H_{10}{=}CHBr$	(52)	1.5132[d]	87	43
$C_6H_5HgCCl_2Br$	Benzaldehyde	$C_6H_5CH{=}CCl_2$	(65)	1.5872[e]	95	65
	Cyclohexanone	cyclo-$C_6H_{10}{=}CCl_2$	(65)	1.5075[f]	95	58
$C_6H_5HgCBr_3$	Benzaldehyde	$C_6H_5CH{=}CBr_2$	(53)	1.6348[g]	92	50

[a] Lit.[23] n_D^{25} 1.5762. [b] Lit.[24] n_D^{20} 1.4620. [c] Lit.[25] n_D^{25} 1.6071 for *trans* isomer. [d] n_D^{25} 1.5130 for sample from $[(C_6H_5)_3PCH_2Br]Br + C_6H_5Li +$ cyclo-$C_6H_{10}{=}O$ reaction. [e] Lit.[12] n_D^{23} 1.5874. [f] Lit.[12] n_D^{20} 1.5096. [g] Lit.[25] n_D^{25} 1.6348.

to the $(C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}X_2$ produced; thus formation of $RR'CX_2$ by-product on reaction with carbonyl compounds is avoided. The sodium trihaloacetate route also avoids this difficulty, but is restricted to the preparation of $RR'C{=}CCl_2$, $RR'C{=}CClF$ and $RR'C{=}CF_2$ from the practical standpoint of starting material availability. No analogous "one-pot" routes to $RR'C{=}CHX$ are known.

At the present time one can only speculate about the mechanism of these reactions. An obvious possibility is a reaction sequence that involves carbene trapping by the phosphine as a discrete step:

$$C_6H_5HgCX_2Br \longrightarrow CX_2 \xrightarrow{(C_6H_5)_3P} (C_6H_5)_3\overset{+}{P}{-}\overset{-}{C}X_2 \xrightarrow{RR'C{=}O} RR'C{=}CX_2$$

However, a direct reaction between mercurial and triphenylphosphine, with or without intervening phosphonium salt formation (→ $[(C_6H_5)_3PCX_2HgC_6H_5]Br$), also is a possibility which must be given serious consideration.

From the present qualitative evidence available we tend to favor the latter alternative. The reactions between phenyl(halomethyl)mercurials and triphenylphosphine appear to go to completion much more rapidly than those occurring between mercurial and olefins. One half hour at 80° was sufficient to cause quantitative formation of phenylmercuric bromide in all cases. One may note that in the case of triphenylphosphine mechanisms other than the carbene mechanism are quite possible. The possibly related radical Michaelis–Arbuzov reaction occurring between $C_6H_5HgCHClBr$ and $C_6H_5HgCCl_2Br$ and phosphite esters[4] supports such a possibility. In any case, the intermediacy of triphenylphosphinehalomethylenes in these reactions seems a certainty. Not only are Wittig reaction products formed when the mercurial-triphenylphosphine reactions are carried out in the presence of aldehydes and ketones, but another experiment shows this as well. When equimolar quantities of triphenylphosphine, phenyl(bromochloromethyl)mercury and sodium tetraphenylborate in ethanol solution were heated at reflux for 15 min, the protonation product of triphenylphosphinechloromethylene, $[(C_6H_5)_3PCH_2Cl][B(C_6H_5)_4]$, was isolated from the solid which precipitated.

EXPERIMENTAL

General comments

All reactions involving preparation or use of organolithiums, phosphinemethylene reagents and halomethylmercurials were carried out under an atmosphere of prepurified nitrogen. Analyses were performed by Dr. S. M. NAGY (M.I.T. Microchemical Laboratory) and the Galbraith Laboratory, Knoxville, Tenn. Infrared spectra were obtained using a Perkin Elmer Model 337 grating spectrophotometer. NMR spectra of the olefinic products also were obtained. They were, in all cases, consistent with the structures indicated.

Preparation of phosphonium halides

(1) *(Hydroxymethyl)triphenylphosphonium bromide.* Triphenylphosphine (0.2 mole) was added in portions to a solution of 0.3 mole of 35 % formalin and 45 ml (0.4 mole) of 48 % hydrobromic acid. The mixture was stirred; after a few minutes the hydroxymethylphosphonium salt began to precipitate. The mixture was allowed to stand for 2 h, and the crystalline product was filtered and washed with acetone to give 51.5 g (69 %), m.p. 202–204°. Recrystallization from isopropyl alcohol gave m.p. 203–205°. (Found: C, 61.16; H, 5.05. $C_{19}H_{18}BrOP$ calcd.: C, 61.16; H, 4.86 %.)

(2) *(Bromomethyl)triphenylphosphonium bromide**. A mixture of 0.10 mole of (hydroxymethyl)triphenylphosphonium bromide and 0.0363 mole of phosphorus tribromide in 100 ml of benzene was heated at reflux for 23 h with stirring. After this time the solution was dark orange and an orange solid was present. The mixture was cooled to room temperature and 80 ml of methanol was added. The solvent was removed at reduced pressure and the residue treated with 100 ml of water to extract the phosphonium salt. The aqueous extracts were saturated with solid potassium bromide and extracted with chloroform. The phosphonium salts were crystallized from the hot, concentrated chloroform solution by addition of ethyl acetate. This

* Procedure developed by Dr. ERWIN HAHN in these laboratories.

procedure gave 26.3 g of product, m.p. 234–239°; recrystallization from methanol–ethyl acetate gave 25.7 g (60%) of product, m.p. 237–240°. An analytical sample, m.p. 242–243.5°, was recrystallized from water. Ramirez *et al.*[18] report m.p. 240–241° (Found: C, 52.14; H, 3.62. $C_{19}H_{17}Br_2P$ calcd.: C, 52.32; H, 3.92%.). A picrate, m.p. 189–190° (from methanol) was prepared (Found: C, 51.47; H, 3.51. $C_{25}H_{19}BrN_3O_7P$ calcd.: C, 51.38; H, 3.28%.). The tetraphenylborate, $[(C_6H_5)_4PCH_2Br][B(C_6H_5)_4]$, had m.p. 214–216° (Found: C, 76.12; H, 5.31. $C_{43}H_{37}BBrP$ calcd.: C, 76.46; H, 5.52%.). More recent work[18,19] has shown that (bromomethyl)triphenylphosphonium bromide may be prepared by the direct reaction of methylene bromide with triphenylphosphine.

(3) *(Iodomethyl)triphenylphosphonium iodide.* A solution of 0.115 mole of triphenylphosphine and 0.15 mole of methylene iodide in 30 ml of benzene in a flask equipped with a reflux condenser and a drying tube and protected from the light by aluminum foil was heated at 45–50°. After a few minutes the solution became cloudy and small crystals formed. After 4 h 18.2 g of white crystals were isolated. A second yield of 12.6 g was isolated after 12 h more at 45°. The product was not very soluble in methanol, isopropyl alcohol, acetone or methylene chloride. It was washed thoroughly with benzene and dried *in vacuo* to give material of m.p. 228–230° (dec.) (turns yellow at about 200°) (Found: C, 43.04; H, 3.23. $C_{19}H_{17}I_2P$ calcd.: C, 43.36; H, 3.45%.). Michaelis[20] had reported that the reaction of triphenylphosphine with methylene iodide gives $[(C_6H_5)_3PCH_2P(C_6H_5)_3]I_2$, m.p. 230–231°. It would appear that his characterization was in error. A tetraphenylborate derivative, $[(C_6H_5)_3PCH_2I][B(C_6H_5)_4]$, was prepared, m.p. 178–179° (from acetone). (Found: C, 71.51; H, 4.90. $C_{43}H_{37}IPB$ calcd.: C, 71.48; H, 5.16%.)

Reaction of (bromomethyl)triphenylphosphonium bromide with phenyllithium

(a) *Cyclohexanone quench.* In a 300 ml three-necked flask equipped with reflux condenser, magnetic stirrer and nitrogen inlet tube was placed 4.83 g (0.011 mole) of phosphonium salt in 50 ml of diethyl ether. To this mixture was added rapidly 10 mmoles of phenyllithium in ether. A deep red-orange color developed immediately. The reaction mixture was stirred for 35 min, at which time it gave a negative Gilman Color Test I[21]. Cyclohexanone (20 mmoles) was added; almost complete discharge of the phosphinemethylene reagent color resulted. The mixture was heated at reflux overnight. Volatile materials were removed by a high vacuum trap-to-trap distillation. The distillate was analyzed by g.l.c. (25% Dow Corning 550 Silicone Fluid on Chromosorb P at 115°) using excess cyclohexanone as the standard. (The cyclohexanone in the distillate was determined independently as the 2,4-dinitrophenylhydrazone). The products were shown to be benzene (53%), methylenecyclohexane (43%), bromobenzene (46%), and (bromomethylene)cyclohexane (46%). The first three were identified by means of their infrared spectra and their g.l.c. retention times (comparison with those of authentic samples). (Bromomethylene)cyclohexane: n_D^{26} 1.5130 (Found: C, 48.29; H, 6.24. $C_7H_{11}Br$ calcd.: C, 48.02; H, 6.33%.). Infrared spectrum (pure liquid): 3075 (m), 2940 (s), 2870 (s), 1720 (w), 1640 (m), 1550 (w), 1450 (s), 1350 (w), 1340 (s), 1325 (m), 1280 (s), 1258 (m), 1227 (s), 1170 (m), 1128 (m), 1100 (w), 1085 (w), 1020 (w), 985 (s), 930 (w), 900 (m), 855 (s), 775 (s), 700 (s), 620 (s) cm^{-1}.

(b) *Benzaldehyde quench.* The phosphinemethylene mixture, prepared as in (a) on the same scale, was quenched with 18.9 mmoles of freshly distilled benzaldehyde.

The reaction mixture was heated at reflux with stirring for 18 h and was worked up as in (*a*). The products were shown by g.l.c. analysis to be benzene (48 %), styrene (~ 2 %), bromobenzene (39 %) and *β*-bromostyrene (48 %). Their identity was proven by comparison of their g.l.c. retention times and infrared spectra with those of authentic samples.

Reaction of (iodomethyl)triphenylphosphonium iodide with phenyllithium

(*a*) *Cyclohexanone quench.* Eleven mmoles of the phosphonium salt was suspended in 50 ml of ether and 10 mmoles of ethereal phenyllithium was added rapidly at room temperature. An orange-yellow solution resulted which became mustard yellow within 2 h. To this solution was added 20 mmoles of cyclohexanone and the reaction mixture was heated at reflux for 8 h with stirring. At the end of this time about one half of the ether was distilled off using a Widmer column; the remaining volatiles were distilled *in vacuo* into a receiver at −78°. G.l.c. analysis of the distillate (Dow Corning 550 Silicone Fluid on Chromosorb P, 111°) showed the presence of benzene (26 %), iodobenzene (73 %), methylenecyclohexane (55 %) and (iodomethylene)cyclohexane (22 %). The first three products were identified by means of their g.l.c. retention times and infrared spectra. (Iodomethylene)cyclohexane: n_D^{26} 1.5623. (Found: C, 37.93; H, 5.20; I, 56.99. $C_7H_{11}I$ calcd.: C, 37.86; H, 4.99; I, 57.15 %.)

(*b*) *Acetone quench.* The same procedure as in (*a*) was used in the reaction of 18.5 mmoles of phosphonium salt with 18.5 mmoles of phenyllithium. To the resulting solution was added 37 mmoles of anhydrous acetone. The mixture solidified to a pasty mass; this was heated at reflux for 25 h. The usual work-up procedure followed. Analysis of the distillate by gas chromatography (TCEP* column at 110°) showed the presence of benzene (38 %), iodobenzene (54 %) and $(CH_3)_2C{=}CHI$ (14 %), as well as larger amounts of mesityl oxide. Isolation of isobutene was not attempted. 1-Iodo-2-methylpropene was identified by analysis. (Found: C, 26.56; H, 3.96; I, 69.51. C_4H_7I calcd.: C, 26.39; H, 3.88; I, 69.73 %.)

Reaction of phenyl(halomethyl)mercurials with triphenylphosphine in the presence of aldehydes

The preparation of 1-chloro-1-octene is described as an example of the procedure used. A solution of 20 mmoles each of triphenylphosphine and phenyl(bromochloromethyl)mercury[3,10] and 40 mmoles of *n*-heptaldehyde in 30 ml of dry benzene was heated slowly to 80° with stirring under an atmosphere of nitrogen. Phenylmercuric bromide began to precipitate even before the benzene began to reflux. The reaction mixture remained light yellow throughout. (Very often, however, in such reactions the mixtures became light-to-dark red, and the color was discharged or lightened considerably when precipitation commenced.) The mixture was heated at reflux for 30 min, cooled and filtered from 6.5 g (91 %) of phenylmercuric bromide. The volatile components of the filtrate were removed by a high vacuum trap-to-trap distillation. The distillation residue was extracted with 200 ml of cyclohexane, and on cooling 4.8 g (87 %) of triphenylphosphine oxide crystallized from the extracts. Recrystallization from this solvent gave a 79 % yield of pure material, identified by its m.p. and mixed m.p. The distillate was concentrated to 7 g using a Widmer column and analyzed by

* TCEP = 1,2,3-triscyanoethoxypropane.

g.l.c. (20% Dow Corning 710 Silicone Fluid on Chromosorb P, 148° jacket temperature, 20 p.s.i. helium, toluene standard) and found to contain 1-chloro-1-octene (yield 81.5%). A mixture of *cis* and *trans* isomers was present, but these were not well resolved and hence the *cis/trans* ratio was not determined accurately. The isomer with longer retention time (presumed *trans*) was favored by about a factor of 2, but in the case of 1-bromo-1-octene prepared by this route a *ca* 1:1 mixture of the *cis* and *trans* isomers was present. Samples of 1-chloro-1-octene were collected by g.l.c.: n_D^{25} 1.4380 (Found: C, 65.76; H, 10.31. $C_8H_{15}Cl$ calcd.: C, 65.53; H, 10.24%.). Infrared spectrum (liquid film): 3170 (w), 2965 (s), 2935 (s), 2870 (s), 1720 (w), 1635 (m), 1470 (s), 1385 (w), 1350 (w), 1300 (w), 1107 (w), 930 (s), 884 (w), 810 (m), 740 (m), 720 (m), 704 (m) cm^{-1}.

Pertinent data concerning other mercurial-phosphine–aldehyde reactions are summarized in Table 1.

Reaction of phenyl(halomethyl)mercurials with triphenylphosphine in the presence of cyclohexanone

The preparation of (dichloromethylene)cyclohexane is described as an example of the procedure used. A solution of 10 mmoles each of triphenylphosphine and phenyl-(bromodichloromethyl)mercury[24] and 50 mmoles of cyclohexanone in 5 ml of *o*-xylene was heated at reflux for 24 h under nitrogen with stirring. Phenylmercuric bromide (3.4 g, 95%) was filtered. The filtrate was distilled *in vacuo* into a receiver at −78° and the distillate was analyzed by g.l.c. (Dow Corning 710 Silicone Fluid on Chromosorb P, jacket at 172°, 15 p.s.i. helium). (Dichloromethylene)cyclohexane was obtained in 65% yield, n_D^{25} 1.5075; lit.[12] n_D^{25} 1.5096. Infrared spectrum (pure liquid): 2980 (m), 2930 (s), 2885 (m), 2850 (s), 1620 (m), 1450 (s), 1330 (w), 1270 (m), 1254 (w), 1230 (s), 1105 (m), 1070 (w), 990 (s), 930 (s), 920 (s), 860 (s), 800 (m) cm^{-1}.

The distillation residue was extracted with boiling cyclohexane; 1.6 g (58%) of triphenylphosphine oxide was isolated.

Reaction of triphenylphosphine with phenyl(bromochloromethyl)mercury in the presence of sodium tetraphenylborate in ethanol

Five mmoles each of the phosphine, the mercurial and sodium tetraphenylborate were dissolved in 50 ml of ethanol. The mixture was heated at reflux for 15 min. A dense white precipitate appeared. The mixture was cooled to room temperature, 100 ml of ethyl acetate was added, and the solid (2.5 g) was filtered. It was recrystallized (methylene chloride–ethyl acetate) to give white solid of m.p. 212–214°. Three further recrystallizations raised the m.p. to 221–222°. A mixture m.p. with authentic $[(C_6H_5)_3PCH_2Cl][B(C_6H_5)_4]$ was not depressed.

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SUMMARY

The action of phenyllithium on (bromomethyl)triphenylphosphonium bromide

results in a nearly equimolar mixture of triphenylphosphinebromomethylene (formal H^+ abstraction) and triphenylphosphinemethylene (formal Br^+ abstraction). With (iodomethyl)triphenylphosphonium iodide a mixture of triphenylphosphineiodomethylene and triphenylphosphinemethylene is formed in which the latter is favored by a factor of about three.

A new route to haloolefins based on phenyl(halomethyl)mercurial reagents is summarized by the equations below (X = Cl and Br).

$$C_6H_5HgCX_2Br + (C_6H_5)_3P + RR'C{=}O \longrightarrow RR'C{=}CX_2 + C_6H_5HgBr + (C_6H_5)_3PO$$

$$C_6H_5HgCHXBr + (C_6H_5)_3P + RR'C{=}O \longrightarrow RR'C{=}CHX + C_6H_5HgBr + (C_6H_5)_3PO$$

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