The Reaction of Lithium Diphenylphosphide and Simple Aryl Halides

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Lithium diphenylphosphide has been found to react with *p*-bromo- and *p*-iodotoluene, *m*-bromotoluene, *p*-bromobiphenyl, and *p*-dibromobenzene producing diphenyl(*p*-tolyl)phosphine, diphenyl(*m*-tolyl)phosphine, diphenyl(*p*-biphenyl)phosphine, and *p*-bis(diphenylphosphino)benzene, respectively, in 70–80% yields. Gas-liquid partition chromatography at 240–300° was used to establish the presence of only one phosphine in each of these reactions. The products were isolated as oxides. Addition of phosphide to aryl halide has been found to lead to little or no tertiary aryl phosphine in the reactions of the tolyl halides, but addition of lithium diphenylphosphide to a mixture of aryl halide and lithium chloride was found to lead to tertiary phosphine in fair to good yields. It was concluded that the reaction does not occur by an elimination–addition mechanism nor a simple halogen–metal interchange. A transition state involving two molecules of lithium diphenylphosphide is suggested in which one molecule of lithium diphenylphosphide coordinates with the halide atom while the other displaces it from carbon.

Although the reaction of alkali metal organophosphides with aryl halides which are unactivated toward nucleophilic displacement has been reported, none of these reports involve monoalkali metal phosphides.[3,4]

$$PhPLi_2 + 2PhBr \longrightarrow Ph_3P + 2LiBr \quad (1)$$

$$[PhPNa]_2 + 2PhBr \longrightarrow [Ph_2P]_2 + 2NaBr \quad (2)$$

No attempt seems to have been made toward elucidation of the mechanism of these reactions. In the course of work on organophosphorus systems an investigation of this problem was undertaken.

Results

It has been found that lithium diphenylphosphide reacts with simple aryl bromides and iodides in tetrahydrofuran at room temperature with the evolution of heat. Diphenylarylphosphines isolable as such or as their oxides are produced in high yields as shown by equation 3. Results are tabulated in Table I.

$$Ph_2PLi + ArX \longrightarrow Ph_2PAr + LiX \quad (3)$$

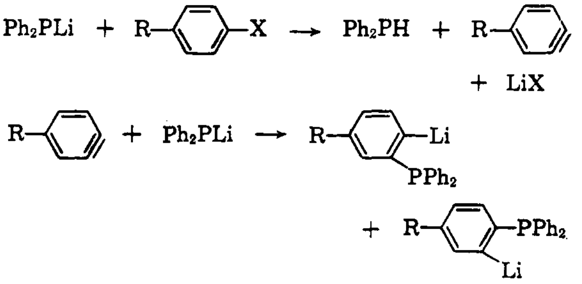
X = bromide or iodide
Ar = *p*-tolyl, *m*-tolyl, *p*-biphenyl, *p*-biphenylene

Gas chromatographic analysis of the reaction mixtures after steam distillation has shown that no diphenyl(*p*-tolyl)phosphine is produced from *m*-bromotoluene and that no *meta* isomer is produced from *p*-bromotoluene. Diphenyl(*p*-tolyl)phosphine has a longer retention time than the *meta* isomer on a silicone DC-200 column. The same is true of the corresponding oxides. This represents, to the best of our knowledge, the first reported separation of positionally isomeric tertiary arylphosphines and oxides by gas–liquid partition chromatography.[5] The same method was employed to demonstrate that only diphenyl(*p*-biphenylyl)phosphine is obtained from the reaction of lithium diphenylphosphide and 4-bromobiphenyl. Higher temperatures and faster flow rates were found necessary to establish that only the known *p*-bis(diphenylphosphino)benzene dioxide resulted from *p*-dibromobenzene. This represents the first use of gas–liquid partition chromatography on diphosphines and their mono- and dioxides.

Discussion

Several paths may be envisaged for the replacement of halide by lithium diphenylphosphide, *e.g.*, through a benzyne mechanism, a halogen–metal interchange, and a displacement on carbon.

There is evidence indicating that lithium diphenylphosphide is too weak a base to abstract an *ortho* hydrogen from simple aryl halides.[6,7] Nevertheless, the possibility of elimination producing an aryne intermediate followed by addition of lithium diphenylphosphide presents itself as a possibility.



(4)

(5)

If *p*-bromotoluene and *m*-bromotoluene were to react by the path shown in equations 4 and 5, isomeric diphenyltolylphosphines would be produced in each case. It would seem, therefore, that elimination–addition does not occur to any extent in the reaction of aryl bromides or iodides and lithium diphenylphosphide.

In view of the work of Brook and Wolfe[8] who showed that halogen–metal interchange is the major path by which simple aryl halides and triphenylsilylpotassium react to form tetraarylsilanes, halogen–metal interchange might be suspected in the present reaction. Halogen–metal interchange would lead to aryllithium and diphenylphosphinous halide. These products could then either react with each other producing tertiary arylphosphine (equation 6) or, if separation of these species beyond reaction distance occurred, they might react with other species in the reaction milieu (equation 7). Since diphenylphosphinous halides are known to react with lithium diphenylphosphide to produce tetraphenylbiphosphine,[4,9] addition of aryl halide to lithium diphenylphosphide might be expected to produce large amounts of tetraphenylbiphosphine

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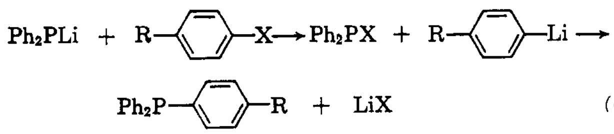
TABLE I

YIELDS OF REACTION OF LITHIUM DIPHENYLPHOSPHIDE WITH ARYL HALIDES[a]

	p-Bromotoluene			p-Iodotoluene			m-Bromotoluene			p-Bromobiphenyl		p-Dibromobenzene
Manner of addition[b]	N	I	I-L[f]	N	I	I-L[f]	N	I	I-L[f]	N	I	N
% Yield of Ph_2POOH[c]	0	60	36	9	47	0	0	65	3	3	4	5
% Yield of product[d]	65	0	38	68	9	57	68	3	65	70	75	75
% Recovery of Ph_3P[e]	12	11	8	6	10	17	8	6	17	7	5	6
% Recovery of Ph_3PO[e]	2	2	9	4	2	7	1	5	12	9	8	8

[a] All per cents are based on starting triphenylphosphine used in the preparation of the phosphide.[6,7] [b] N refers to normal addition which is dropwise addition of aryl halide to a refluxing solution of phosphide, I signifies inverse addition or addition of phosphide to aryl halide, and I–L indicates inverse addition of phosphide to a solution of the halide containing lithium chloride. [c] Calculated from weight of material isolated and characterized by infrared and mixture melting points. [d] Refers to combined phosphine and corresponding oxide. Over 75% of the reported yields represent oxide isolated in pure form and characterized by infrared spectral comparison, gas chromatographic retention time comparison, and mixture melting point with material prepared from the corresponding organometallic and diphenylphosphinous chloride followed by oxidation. The remaining portion of the reported yield was obtained from quantitative gas chromatographic analysis of remaining fractions after isolation of the major portion of product. This was cross checked by gas chromatographic analysis before isolation. [e] Calculated from gas chromatographs of the remaining fractions after isolation of the major portion of product and cross checked by gas chromatographic analysis of the reaction mass before isolation of product. These materials were present from the preparation of the lithium diphenylphosphide as described in the Experimental section.[6,7] [f] The apparent high material balance in these cases is probably due to the presence of lithium halides in the acetone solution (possibly complexed with the phosphines and oxides) which are not determined gas chromatographically but add to the total weight.



(6)

$$Ph_2PX + Ph_2PLi \longrightarrow (Ph_2P)_2 + LiX \qquad (7)$$

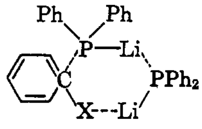
$$(Ph_2P)_2 + 3H_2O_2 \longrightarrow 2Ph_2POOH + 2H_2O \qquad (8)$$

and correspondingly low yields of tertiary arylphosphine.

The tetraphenylbiphosphine would show up as diphenylphosphinic acid after oxidation,[4] as shown in equation 8. As can be seen from Table I, very little phosphinic acid was produced on normal addition. This result, accompanied by the high yields of tertiary aryl phosphines, would seem to negate the possibility of halogen–metal interchange followed by separation of the primary products. Furthermore, addition of carbon dioxide has not led to isolation of toluic acids.[10]

If halogen–metal interchange is occurring to any extent, it would seem that inverse addition should lead to higher yields of product and correspondingly lower yields or phosphinic acid than normal addition. As shown in Table I inverse addition of the reagents has been found, in the reactions of *para-* and *meta-*tolyl bromides and iodides, to lead to very little or no product. Most of the phosphorus appears as phosphinic acid. This acid does not arise from the oxidative hydrolysis of unchanged lithium diphenylphosphide upon steam distillation. The red color of the latter species is discharged upon addition of the phosphide to the tolyl halide. Accumulated lithium diphenylphosphide would be expected to react with the aryl halide during the reflux period. This was shown by mixing the reagents at a temperature low enough for little or no reaction to occur (0–10°) and allowing the mixture to come to reflux. Under these conditions the same results were obtained as when normal addition was employed. It appears that other path(s) of reaction are open to the reagents. Low concentrations of lithium diphenylphosphide favor these, as yet undisclosed, paths over the replacement reaction.

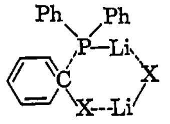
The possibility that a transition state, I, involving two molecules of lithium diphenylphosphide and one of aryl halide, is essential to the replacement of halide is consistent with the difference in results between normal and inverse addition. The role of the second molecule of phosphide would involve the complexing action of the lithium ion, which has a high charge density, with the aryl halide. Another way of visualizing this concept is that the reaction mechanism is of the "push-pull" type.



I

Issleib and Tzschach[11] have concluded from molecular weight determinations that lithium diphenylphosphide is present as a dimeric associated complex in dioxane solution.

The presence of lithium chloride in the solution of lithium diphenylphosphide must be considered. This salt arises in the preparation of lithium diphenylphosphide from triphenylphosphine, lithium, and *t*-butyl chloride.[5,6] Lithium chloride may take the place of one of the two molecules of phosphide. Furthermore, we would expect it to be a better complexing agent. Addition of the diphenylphosphide reagent to a solution of tolyl halide containing lithium chloride was carried out. As Table I indicates, this gave results closer to those obtained upon normal addition.



II

Experimental

1. **Preparation of Lithium Diphenylphosphide.**[6,7] A solution of 2.1 g. (0.3 g.-atom) of lithium ribbon and 26.2 g. (0.1 mole) of triphenylphosphine in 150 ml. of tetrahydrofuran was allowed to react under nitrogen with agitation for 3 hr. After addition of

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(10) There remains the possibility of very rapid reaction of the aryllithium and halophosphine formed in a halogen–metal interchange.

(11) K. Issleib and A. Tzschach, *Chem. Ber.*, **92**, 1118 (1959).

9.3 g. (0.1 mole) of *t*-butyl chloride and heating to reflux for 10 min., the reaction mass was allowed to cool to ambient temperature and transferred under nitrogen to a dropping funnel on a second vessel under nitrogen.

2. **General Procedure Used in the Reaction of Lithium Diphenylphosphide with Aryl Halides. Method A. Normal Addition.**—The red reaction solution from 1 was allowed to run rapidly into the vessel leaving unchanged metal in the funnel. After the dropping funnel was replaced, the solution was heated to reflux and a solution of the aryl halide in tetrahydrofuran was added dropwise with rapid stirring under nitrogen.

Method B. Inverse Addition.—The red reaction solution was allowed to drop slowly into a rapidly stirred, refluxing solution of the aryl halide in tetrahydrofuran under nitrogen.

After addition was complete the reaction mixture was refluxed for 2 hr. and then allowed to return to ambient temperature. The flask was opened to air, most of the tetrahydrofuran distilled, and the residual mass steam distilled. After cooling the residue, the supernatant aqueous layer was separated from the bottom oily layer by extraction with chloroform. Acidification of the basic aqueous layer precipitated most of the phosphinic acid in it. This accounted for most of the phosphinic acid produced with little additional acid being isolated after treatment with 3% hydrogen peroxide at a later stage in the work-up.

The chloroform layer was then subjected to gas chromatographic analysis. The instrument was a Research Specialties Model 60-1A gas chromatograph with a flame ionization detector operating at 240–290°, which contained a 3-ft. column of 5% silicone oil DC-200 on 80–100-mesh Chromasorb (W-AW). In all cases a small amount of triphenylphosphine and its oxide were present. These materials presumably arose from uncleaved triphenylphosphine in the initial step. The per cent of uncleaved triphenylphosphine (calculated from chromatographic curve areas and conversion ratios arrived at from mixtures of known compositions) was usually between 10 and 15%.

The chromatographs of this chloroform solution showed peaks due to triphenylphosphine, triphenylphosphine oxide, small peaks of short retention times (due to unknown components and diphenylphosphine), and only two other peaks. These two were shown to be due to the phosphine and phosphine oxide expected from direct substitution of halide by the diphenylphosphide group.

Evaporation of the chloroform solution and dissolution of the remaining semisolid in acetone followed by addition of 3% hydrogen peroxide solution gave a clear solution which was allowed to stand overnight. The addition of peroxide was accompanied by heat evolution in most cases. Concentration of this solution, followed by addition of water and reconcentration, removed the acetone and produced a precipitate of semisolid. The supernatant aqueous layer was acidified after decantation and any precipitating phosphinic acid was isolated. Acetone trituration of water-insoluble material separated any remaining phosphinic acid as insoluble solid. The acetone filtrate solution was subjected to gas chromatographic analysis which, in most cases, disclosed peaks representing solvent, a small amount of triphenylphosphine, an even smaller amount of triphenylphosphine oxide, and a very large peak due to the diphenylarylphosphine oxide produced. Curve areas, conversion factors, and the weight of solid obtained on evaporation of acetone were used to calculate crude yields. Isolation of product in pure form was accomplished by crystallization.

3. **Preparation of Diphenyl(*m*-tolyl)- and Diphenyl(*p*-tolyl)-phosphines.**—The infrared spectra of the tolylphosphine oxides was that expected for *meta* and *para* isomers, respectively. The melting points of the isolated materials were identical with those reported in the literature.[12]

4. **Preparation of Diphenyl-*p*-biphenylphosphine Oxide.**—Diphenyl-*p*-biphenylphosphine oxide (m.p. 143–144°), previously unreported, showed no depression of mixture melting points with material prepared from the corresponding organometallic and diphenylphosphinous chloride, followed by oxidation. The two materials also had identical retention times under the conditions mentioned in connection with gas chromatographic separation of the isomeric tolyl oxides; their infrared spectra were identical.

Anal. Calcd. for $C_{24}H_{19}PO$: C, 81.4; H, 5.37; P, 8.75. Found: C, 81.71; H, 5.45; P, 8.28.

5. **Preparation of *p*-Bis(diphenylphosphino)benzene Dioxide.**—*p*-Dibromobenzene led, on normal addition, to *p*-bis(diphenylphosphino)benzene dioxide as shown by analysis, mixture melting points and infrared spectral comparison with the known material.[13,14] Gas–liquid partion chromatography at 320° employing very rapid carrier gas flow indicated that the crude reaction mixture contained only one diphosphine, the corresponding monoxide, and dioxide.

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Aluminum Chloride-Induced Halogen Exchange of Alkyl Halides

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Halide exchange between *n*-propyl bromide or *n*-propyl iodide and aluminum chloride yields, initially, an exchange product containing a high per cent of *n*-propyl chloride. Interchange of halogen between ethyl and *n*-propyl halides, catalyzed by aluminum chloride, also gives initial exchange products rich in the *n*-propyl halide. An equilibrium constant for the exchange of propyl bromide with aluminum chloride is estimated and mechanistic implications of the results are considered.

Although much work has been done on aromatic substitution by means of the Friedel–Crafts, aluminum trichloride-catalyzed reaction, relatively little attention has been given to halogen exchange between alkyl halides and aluminum trichloride.

Isotopic studies reveal that alkyl and acyl halides will exchange halogen atoms with the corresponding aluminum trihalides,[1,2] and interchange of methyl halides with aluminum halides has been studied.[3] Aluminum trihalide also may catalyze exchange of halogen between one alkyl halide and another[4]; thus a mixture of carbon tetrachloride, ethyl iodide, and aluminum chloride affords carbon tetraiodide.[5] Recent

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