Phosphides and Arsenides as Metal–Halogen Exchange Reagents. Part 2. Reactions with Aromatic Dihalides[1,2]

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1,2-Dihalogenobenzenes react with two molar equivalents of lithium diphenylphosphide in the presence of furan to give, after oxidation, triphenylphosphine oxide (major) and the corresponding 2-halogenophenyldiphenylphosphine oxide. No trace of furan–dehydrobenzene adduct was observed in these reactions; however, 1- and 2-naphthyldiphenylphosphine oxides (9 : 4) were detected. These compounds were the major products from the reaction of the furan–dehydrobenzene adduct with diphenylphosphide, although the ratio of 1- to 2-isomers was quite different (1 : 9) in this case.

Reaction of lithium diphenylphosphide with 3,4-dichloronitrobenzene gave tetrachloroazobenzene (40%) as the only isolated product and attempts to replace 1,2-dihalogenobenzenes with 2-halogenobenzenediazonium salts gave much lower yields of products. Although dehydrobenzene is thought to be involved in many of these reactions, alternative mechanisms also operate, depending on the halides used.

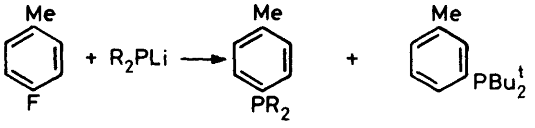
The reaction of lithium diphenylarsenide with 1,2-dihalogenobenzenes gave triphenylarsine as the major product and it seems likely that similar mechanisms to those involved in reactions of diphenylphosphide are operating. Surprisingly, dehydrobenzene–furan adduct reacted with diphenylarsenide to give naphthalene in high yield.

In our continuing investigation of phosphide and arsenide anions as metal-halogen exchange reagents,[2] reactions with 1,2-dihalogenobenzenes were of interest since they offered a potential route to dehydrobenzene. Organolithium[3] and lithium dialkylamide[4] reagents have been widely used to generate dehydrobenzene from both halogenobenzenes and 1,2-dihalogenobenzenes[5] *via* 2-halogenophenyl anions. Unfortunately further reaction of the organometallic reagent with dehydrobenzene usually occurs.[6]

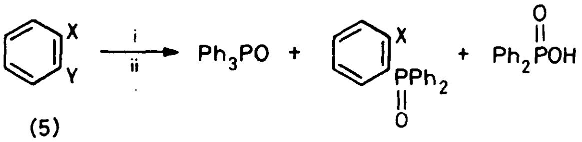
Lithium di-t-butylphosphide has been used as the base to generate dehydrobenzene from 3-fluorotoluene;[7] however, the isolated products are tertiary phosphines (1) and (2), derived from addition of phosphine (or phosphide) to the reactive intermediate. The less sterically hindered di-n-butyl- and diethyl-phosphides react by direct substitution of halide to give only compounds (3) and (4), respectively. Evidence for the attack of phosphide on halogen is available from the isolation of tetra-t-butyldiphosphine from the reaction of 3-bromotoluene with lithium di-t-butylphosphide.[7]

Results and Discussion

(*a*) *Reactions of Diphenylphosphide with* 1,2-*Dihalogenobenzenes*.—A variety of *o*-dihalogenobenzenes (5a—f) were allowed to react with lithium diphenylphosphide (2 mol equiv.) in the presence of a five-fold excess of furan (Scheme 1). Following an oxidative work-up procedure, triphenylphosphine oxide was the major product and 2-halogenophenyldiphenylphosphine oxides were minor products in all of these reactions (Table 1). In no case was the biphenylene (6), the dehydrobenzene–furan adduct (7), naphthalene, or naphthol observed, even by g.l.c. using conditions under which 0.05% of these products can be detected. However, from the reaction with 1,2-dibromobenzene a mixture of 1- and 2-naphthyldiphenylphosphine oxides (9 and 4% respectively by h.p.l.c.) could be isolated. Traces of these compounds could also be detected in similar reactions with 1,2-dichloro- and 1,2-di-iodobenzene, but not in those with mixed halides (5d—f). A similar reaction with 3,4-dichloronitrobenzene followed a quite different route and the only product isolated was 3,3′,4,4′-tetrachloroazobenzene.



(1) R = Bu^t (2)
(3) R = Bu^n
(4) R = Et



(5)

a; X = Y = Cl
b; X = Y = Br
c; X = Y = I
d; X = F, Y = Br
e; X = Cl, Y = Br
f; X = Br, Y = I

Scheme 1. *Reagents:* i, Ph_2PLi; ii, H_2O_2/H_2O

Since appreciable amounts of unchanged 1,2-dihalogenobenzenes were recovered from reactions of two molar equivalents of phosphide with the halides (5), 1,2-dibromobenzene was allowed to react under similar conditions with three molar equivalents of phosphide. Although this caused a reduction in the amount of 1,2-dibromobenzene recovered, it also reduced the yields of all detected products.

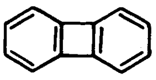
Our failure to detect the dehydrobenzene–furan adduct (7) does not necessarily exclude dehydrobenzene as an intermediate in these reactions. The adduct (7) is known to react with certain nucleophiles to give hydronaphthalene deri-

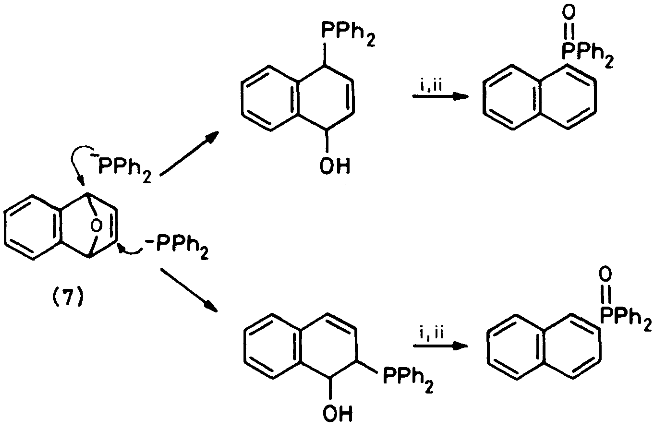
Table 1. Yields of phosphine oxides obtained from the reaction of lithium diphenylphosphide with *o*-dihalogenobenzenes and *o*-halogenobenzenediazonium tetrafluoroborates after oxidation

$$o\text{-}XC_6H_4Y + 2\,LiPPh_2 \longrightarrow Ph_3PO + o\text{-}XC_6H_4P(O)Ph_2 + o\text{-}YC_6H_4P(O)Ph_2$$

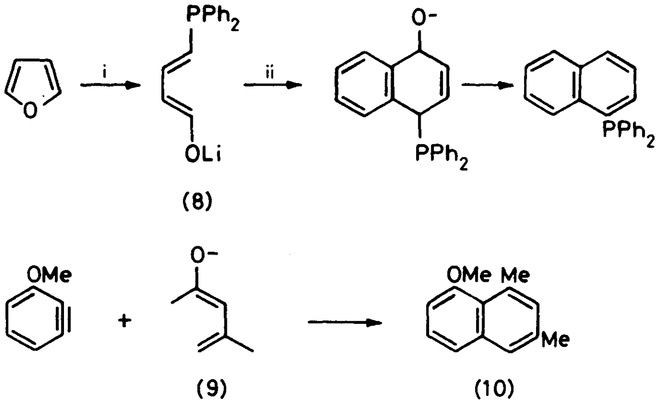
X	Y	Added furan	o-XC$_6$H$_4$Y Unchanged (%)	Yield (%) Ph_3PO	Yield (%) o-XC$_6$H$_4$P(O)Ph$_2$	Yield (%) o-YC$_6$H$_4$P(O)Ph$_2$
Cl	Cl	Yes	14	17	0.3	
Br	Br	Yes	29	39	0.8	
I	I	Yes	49	10	0.2	
Cl	Br	Yes	0	58	Trace	Trace
Cl	Br	No	0	42	Trace	Trace
F	Br	Yes	0	30	Trace	*a*
F	Br	No	0	31	Trace	*a*
I	Br	Yes	0	33	*a*	Trace
I	Br	No	0	11	*a*	Trace
N_2^+	Cl	Yes	0	0		0.3
N_2^+	Br	Yes	0	0.3		*a*
N_2^+	I	Yes	0	10		*a*

[a] Not detected.


(6)



Scheme 2. *Reagents:* i, $-H_2O$; ii, H_2O_2



Scheme 3. *Reagents:* i, Ph_2PLi; ii, dehydrobenzene

vatives [8,9] and it seemed likely that it would react with excess of phosphide in a similar way. Indeed, compound (7) was refluxed with an equimolar quantity of lithium diphenylphosphide to give after oxidation a 1 : 9 mixture of 1- and 2-naphthyldiphenylphosphine oxides in good yield (Scheme 2). However, the quite different ratio (9 : 4) of 1- to 2-naphthyldiphenylphosphines obtained from the reaction of phosphide with aromatic dihalides (5) in the presence of furan, suggests that a different or additional mechanism is operating in these cases. One possible explanation is that furan undergoes ring-opening by phosphide to give (8) * (Scheme 3). Analogous dienolate anions [*e.g.* (9)] are known to react with dehydrobenzenes to give naphthalene derivatives [*e.g.* (10)] [10] and a similar reaction with (8) would give exclusively 1-naphthyldiphenylphosphine.

In the presence of strong base diphenylisobenzofuran (DPB) (11) is reported [9] to be a more satisfactory trapping agent than furan for dehydrobenzene. However, a reaction of phosphide with 1,2-dibromobenzene in the presence of DPB gave only traces of 9,10-diphenylanthracene and its 9,10-endoperoxide (12), the major product being 1,2-dibenzoylbenzene which is presumably † formed from the reaction of DPB with hydrogen peroxide during work-up.

The isolation of (biphenyl-2-yl)diphenylphosphine oxide (13) from the reaction of phosphide with biphenylene (6) suggests that (13) is formed by this route in the reactions of compound (5) with phosphide.

Scheme 4 summarizes the mechanisms possibly operating in the reactions of phosphide with the dihalides (5). The absence of halide containing products, apart from (15), suggests that base-mediated routes [7] to dehydrobenzene intermediates (14) are not important.‡ The isolation of triphenylphosphine oxide, 95% monodeuteriated, from experiments which were quenched with D_2O before peroxidation, implicates the anion (16) and the attempted trapping experiments provide indirect evidence for the formation of dehydrobenzene.

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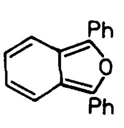
* Tetrahydrofuran is known to undergo an analogous reaction with diphenylphosphide to give 4-hydroxybutyldiphenylphosphine (K. B. Mallison and F. G. Mann, *J. Chem. Soc.*, 1965, 4115).

† The feasibility of this route was confirmed by a separate experiment.

‡ This is supported by reports that lithium diphenylphosphide is not sufficiently basic to deprotonate halogenobenzenes (A. M. Aguiar, H. J. Greenberg, and K. E. Rubenstein, *J. Org. Chem.*, 1963, **28**, 2091).



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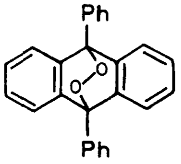

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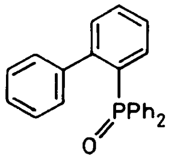

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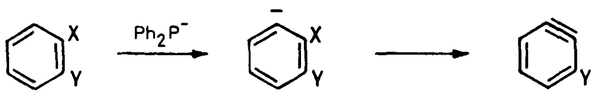

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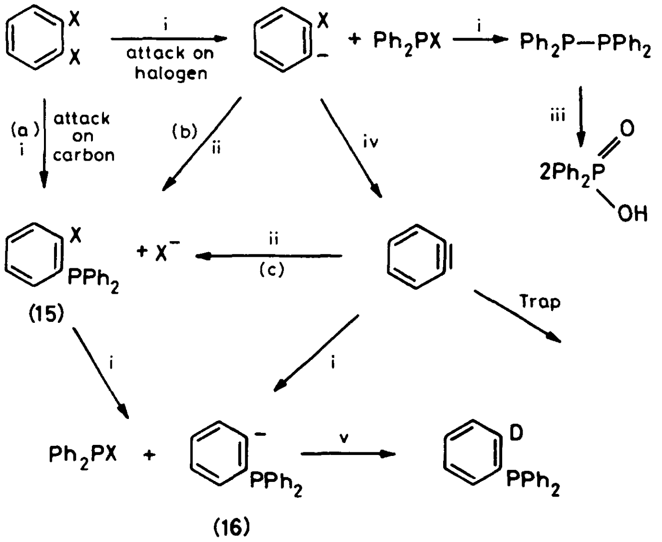
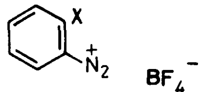


Scheme 4. *Reagents:* i, Ph_2P^-; ii, Ph_2PX; iii, H_2O; iv, $-X^-$; v, D_2O

We have shown * that 2-chlorophenyldiphenylphosphine is formed when dehydrobenzene is generated in the presence of chlorodiphenylphosphine and nucleophilic addition to dehydrobenzene is well documented.[11]

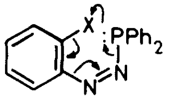
It seems likely that some, or all, of the alternative routes shown in Scheme 4 operate depending on which halide is reacting. In this connection the reaction of 1,2-dibromobenzene with *sodium* diphenylphosphide in the presence of furan is informative. Unlike the analogous reaction with *lithium* diphenylphosphide, no naphthyldiphenylphosphine oxide was formed, although comparable yields of triphenylphosphine oxide and 2-bromophenyldiphenylphosphine oxide were obtained. These results suggest that a dehydrobenzene mechanism is *not* operating in this case, which is in agreement with the reduced polarisability expected for sodium compared to *lithium* phosphide.†

The experiments with mixed halides (5d—f) suggest that reaction *via* dehydrobenzene (Scheme 4, route c) is *not* a major route in the formation of 2-halogenophenylphosphines, since this should lead to a product with the most polarisable halogen atom attached to the phenyl substituent.



(17)

a; X = Cl
b; X = Br
c; X = I



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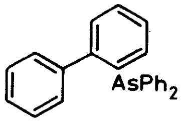
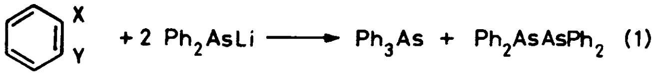


(19)

2-Halogenobenzenediazonium salts (17) appeared to offer an attractive alternative to 1,2-dihalogenobenzenes in these experiments since, in addition to (a) initial attack of phosphide on halogen and (b) direct substitution of halogen and reactions analogous to those in Scheme 4, initial attack on nitrogen to give compound (18) is also possible. This intermediate might offer a more efficient route to dehydrobenzene *via* intramolecular elimination of nitrogen and halogenophosphine.

Disappointingly, reactions of 2-chloro- (17a) and 2-bromo- (17b) diazonium tetrafluoroborates with lithium diphenylphosphide in the presence of furan gave only traces of isolable products (see Table 1). A similar reaction with the 2-iodo compound (17c) gave larger amounts (10%) of triphenylphosphine oxide and a major product, a non-crystalline material which we have been unable to identify.

(*b*) *Reactions of Diphenylarsenide with* 1,2-*Dihalogenobenzenes*.—The major products obtained from reactions of the dihalogenobenzenes (5) with lithium diphenylarsenide were triphenylarsine and tetraphenyldiarsine together with recovered dihalide [equation (1)], the amount of this last product depending on the dihalide used. These results are summarised in Table 2. The yields of triphenylarsine were generally higher than those of triphenylphosphine oxide obtained from the analogous reactions with diphenylphosphide. Trace amounts of 2-halogenophenyldiphenylarsines, (biphenyl-2-yl)diphenylarsine (19) and, from reactions in the presence of furan, naphthyldiphenylarsine and naphthalene, were also isolated. Mechanistic pathways analogous to those outlined in Scheme 4 for phosphide are available for arsenide reactions.



$$C_6H_4XY + 2\,Ph_2AsLi \longrightarrow Ph_3As + Ph_2AsAsPh_2 \quad (1)$$

(5a—f)

A reaction of the dehydrobenzenefuran adduct (7) with lithium diphenylarsenide gave, in contrast to a similar reaction with phosphide, a high yield of naphthalene and an unidentified hydrocarbon.‡ At first sight, arsenide would seem less

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* The dependence of this reaction on the nature of the dehydrobenzene precursor is probably a function of the concentration of dehydrobenzene.

† Recent ^{31}P and ^{7}Li n.m.r. spectroscopic studies suggest that lithium diphenylphosphide is a covalent dimer at least at low temperatures (I. J. Colquhoun, H. C. E. McFarlane, and W. McFarlane, *J. Chem. Soc., Chem. Commun.*, 1982, 220).

‡ This latter compound was not detected in reactions of arsenide with dihalides (6).

Table 2. Yields of tertiary arsines obtained from the reaction of lithium diphenylarsenide with *o*-dihalogenobenzenes

$$o\text{-}XC_6H_4Y + 2\,LiAsPh_2 \longrightarrow Ph_3As + o\text{-}XC_6H_4AsPh_2 + o\text{-}YC_6H_4AsPh_2$$

X	Y	Furan added	*o*-XC_6H_4Y Unchanged (%)	Yield (%)		
				Ph_3As	*o*-$XC_6H_4AsPh_2$	*o*-$YC_6H_4AsPh_2$
Cl	Cl	Yes	48	45	Trace	
Br	Br	Yes	13	66		
I	I	Yes	18	16		
Cl	Cl	No	46	49		
Br	Br	No	21	75		
F	Br	Yes	1	29	Trace	Trace
Cl	Br	Yes	32	33	Trace	Trace
I	Br	Yes	46	14		Trace
F	Br	No	1	59	Trace	Trace
Cl	Br	No	14	73	Trace	Trace
I	Br	No	40	43		Trace

likely to directly deoxygenate the adduct (7) than would phosphide, and the mechanism for naphthalene formation remains obscure.

Experimental

The instruments and general conditions used are described in the first part of this series.[2] Ether refers to diethyl ether.

Reactions of o-*Dihalogenobenzenes with Lithium Diphenylphosphide in the Presence of Furan.*—Lithium diphenylphosphide (0.02 mol) was prepared in the previously described manner from diphenylphosphine (3.72 g, 0.02 mol) and n-butyl-lithium (1.28 g, 0.02 mol) in tetrahydrofuran (THF) (50 cm^3). To the refluxing phosphide solution was added the relevant dihalogenobenzene (0.01 mol) in redistilled furan (10 cm^3). The mixture was refluxed for 3 h and worked up as before.[2] All the dihalogenobenzene–phosphide reactions produced diphenylphosphinic acid (isolated by trituration of the reaction mixture with acetone) and traces of a compound, *m/z* 402 ($Ph_2P_2O_2$). The reaction products were analysed by g.l.c. (F-11 2 m, 2½% SGR, 120 °C) for evidence of 1,4-dihydro-1,4-epoxynaphthalene (7) (R_t 6.4 min) and for unchanged dihalide. No furan adduct was detected in any of these cases. The products were chromatographed (silica gel). Pentane elution gave the dihalides and ethyl acetate gave triphenylphosphine oxide, m.p. 156—157 °C (lit.,[12] 156 °C) together with traces of the relevant *o*-halogenophenyldiphenylphosphine oxide and naphthyldiphenylphosphine oxides. The yields of the phosphine oxides were determined by g.l.c. (2 m 2½% SGR, 245 °C; R_t, triphenylphosphine oxide 9.6 min, *o*-chlorophenyldiphenylphosphine oxide 14.5 min, *o*-bromophenyldiphenylphosphine oxide 18.8 min, and *o*-iodophenyldiphenylphosphine oxide 24 min) or by high pressure liquid chromatography (h.p.l.c.) for the naphthyl derivatives (Spectraphysics 350, 3 mm × 250 mm, 5μ spheresorb silica, 1.2 cm^3/min, 40% chloroform–pentane). A peak on the g.l.c. charts of shorter retention time than triphenylphosphine oxide was shown by the combined g.l.c.–mass spectrum to be $Ph_2P(O)C_4H_7O$.

1,2-*Dichlorobenzene.* This compound gave unchanged dichloride (14%), triphenylphosphine oxide (17%), *o*-chlorophenyldiphenylphosphine oxide (0.3%), m.p. 119—120 °C (lit.,[13] m.p. 123—124 °C), and traces of naphthyldiphenylphosphine oxides.

1,2-*Dibromobenzene.* This compound gave unchanged dibromide (29%), triphenylphosphine oxide (39%), *o*-bromophenyldiphenylphosphine oxide (0.8%), m.p. 136—137 °C (chloroform–pentane) (Found: C, 60.55; H, 4.1; Br, 22.3. Calc. for $C_{18}H_{14}BrOP$: C, 60.53; H, 3.95; Br, 22.37%); $\nu_{max.}$ (KBr) 1 170 cm^{-1}; *m/z* 358, 356, and 201; 1-naphthyldiphenylphosphine oxide (9%), and 2-naphthyldiphenylphosphine oxide (4%).

1,2-*Di-iodobenzene.* This compound gave unchanged diiodide (49%), triphenylphosphine oxide (10%), *o*-iodophenyldiphenylphosphine oxide (0.2%), and traces of naphthyldiphenylphosphine oxides.

Deuterium incorporation in the reaction of 1,2-*dibromobenzene with phosphide.* Deuterium oxide (10 cm^3) was added to the reaction mixture as soon as it cooled. Work-up as before gave triphenylphosphine oxide (36%), which mass spectrometry showed to be 95% monodeuteriated.

1,2-*Dibromobenzene and phosphide at* 0 °C. The phosphide solution was cooled in an ice-bath and the dibromide added while the temperature was kept at 0 °C. No furan–benzene adduct was detected by g.l.c.

1,2-*Dibromobenzene and Three Equivalents of Lithium Diphenylphosphide.*—The addition of dibromide to a refluxing phosphide solution in THF followed by the standard work-up gave triphenylphosphine oxide (32%), dibromide (11%), and traces of naphthyldiphenylphosphine oxides. No adduct could be detected.

1,2-*Dibromobenzene with Two Equivalents of Sodium Diphenylphosphide.*—The reaction was carried out under reflux in a similar way to those with lithium phosphide. Triphenylphosphine oxide (18%) and unchanged dibromide (37%) were detected. There was no trace of furan adduct or naphthyldiphenylphosphine oxides.

Reaction of Chlorodiphenylphosphine with Dehydrobenzene.—Benzenediazoniumcarboxylate [prepared from anthranilic acid (0.011 mol)][14] was treated, as a suspension in chloroform, with chlorodiphenylphosphine (0.72 g, 0.0033 mol) and refluxed for 4 h. The mixture was then cooled, treated with 6% hydrogen peroxide (100 cm^3) and stirred overnight. Chromatography (silica gel) of chloroform extracts of the product gave no trace of phosphine oxides.

The reaction was repeated using diphenyliodonium-2-carboxylate as a benzyne precursor. Chlorodiphenylphosphine (0.5 g, 0.023 mol) and the carboxylate (1.8 g, 5.6 mol) were refluxed for 2 h in dry diglyme. The product was peroxidised, extracted and chromatographed as before. After elution with pentane and then ether, ethyl acetate gave white crystals of *o*-chlorophenyldiphenylphosphine oxide (0.07 g, 10%), m.p. 118—120 °C (chloroform–light petroleum) (lit.,[13] 123—124

°C); *m/z* 314(12%), 313(45), 312(60), 311(100), 201(10), and 199(14).

Reactions of Mixed Dihalogenobenzenes with Lithium Diphenylphosphide.—These reactions were carried out with and without furan. No furan adduct was detected in any of these cases nor was there any unchanged dihalide.

Reactions of Mixed Dihalides with Phosphide in the Presence of Furan.—These all gave small amounts (0.5%) of naphthyldiphenylphosphine oxide.

2-*Bromofluorobenzene.* This compound gave triphenylphosphine oxide (30%) and a trace of a compound which from its mass spectrum [*m/z* 296 (M^+)] appears to be *o*-fluorophenyldiphenylphosphine oxide.

2-*Bromochlorobenzene.* This compound gave triphenylphosphine oxide (58%) together with traces of *o*-bromo- and *o*-chloro-phenyldiphenylphosphine oxide.

2-*Bromoiodobenzene.* This compound gave triphenylphosphine oxide (33%) and traces of *o*-bromophenyldiphenylphosphine oxide.

Reactions of Mixed Dihalides with Phosphide in the Absence of Furan.—In all cases traces of biphenyl-2-yldiphenylphosphine oxide, m.p. 149—151 °C, were isolated by column chromatography (silica gel, ether). The structure of this compound was confirmed by comparison (m.p., mixed m.p. and i.r.) with the product of peroxide oxidation of biphenyl-2-yldiphenylphosphine.[15] The same halogeno substituted phosphine oxides were detected as those found in the presence of furan.

2-*Bromofluorobenzene.* This compound gave triphenylphosphine oxide (31%).

2-*Bromochlorobenzene.* This compound gave triphenylphosphine oxide (42%).

2-*Bromoiodobenzene.* This compound gave triphenylphosphine oxide (11%).

Preparation of 1,4-*Dihydro*-1,4-*epoxynaphthalene.*—3-Methylbutyl nitrite (20 cm^3) in dry dimethoxyethane (20 cm^3) and anthranilic acid (13.7 g, 0.1 mol) in dry dimethoxyethane (45 cm^3) were added dropwise and simultaneously to a refluxing solution of furan (50 cm^3) and dimethoxyethane (50 cm^3). After 1½ h the mixture was cooled and made alkaline with dilute sodium hydroxide. The product was extracted with light petroleum (b.p. 40—60 °C), dried ($MgSO_4$) and evaporated to give 1,4-dihydro-1,4-epoxynaphthalene, m.p. 53—55 °C (lit.,[16] 55—56 °C).

Reaction of 1,4-*Dihydro*-1,4-*epoxynaphthalene with Lithium Diphenylphosphide.*—1,4-Dihydro-1,4-epoxynaphthalene (0.36 g, 0.0025 mol) in THF (25 cm^3) was added to a refluxing phosphide solution (0.0025 mol) in THF (20 cm^3). The mixture was refluxed for 1 h and worked up in the usual manner. No furan adduct remained in the product (g.l.c.). Chromatography on silica gel (ether) gave white crystals (0.5 g, 61%), m.p. 115—117 °C (ethyl acetate); *m/z* 329(16%), 328(76), 327(100), 251(9), 249(15), 201(8), 128(6), and 127(15). H.p.l.c. (conditions as above) showed the presence of 1- and 2-naphthyldiphenylphosphine oxides in the ratio 1 : 9.

Preparation of 1-*Naphthyldiphenylphosphine Oxide.*—To a Grignard reagent prepared from magnesium (3.04 g, 0.125 mol) and 1-bromonaphthalene (22.7 g, 0.1 mol) in THF (50 cm^3), chlorodiphenylphosphine (11.0 g, 0.05 mol) was slowly added. The resulting solution was refluxed for 6 h and the excess of Grignard destroyed (aqueous ammonium chloride). Hydrogen peroxide (50 cm^3, 6%) was added and the mixture stirred for 3 h. Chloroform extraction gave a crude product which gave naphthalene, m.p. 78—80 °C on sublimation. The residue was crystallised from ethyl acetate to give 1-naphthyldiphenylphosphine oxide (40%), m.p. 181—182 °C (lit.,[17] 178—179 °C), *m/z* 329(9%), 328(48), 327(100), 249(15), 202(13), 201(5), 128(5), and 127(7); δ($CDCl_3$) 8.59 (1 H, m) and 7.49 (16 H, m).

Preparation of 2-*Naphthyldiphenylphosphine Oxide.*—A similar reaction of the Grignard from 2-bromonaphthalene (22.7 g, 0.1 mol) gave, after chromatography on silica gel (pentane), naphthalene (0.2 g) and 2,2′-binaphthyl (1.9 g), m.p. 183—185 °C (lit.,[18] 189 °C). Elution with ethyl acetate–light petroleum (b.p. 40—60 °C) (1 : 1) gave 2-naphthyldiphenylphosphine oxide (1.6 g), m.p. 116—117 °C (Found: C, 80.2; H, 5.2; P, 9.85. Calc. for $C_{22}H_{17}OP$: C, 80.48; H, 5.18; P, 9.45%); $\nu_{max.}$ (Nujol mull) 1 440, 1 180, 1 115, and 1 100 cm^{-1}; *m/z* 329(17%), 328(77), 327(100), 201(5), 199(7), and 127(11); δ($CDCl_3$) 7.31—7.83 (m).

Reaction of Biphenylene with Lithium Diphenylphosphide.—Biphenylene[19] (0.76 g, 0.005 mol) was dissolved in THF in a 10-cm^3 volumetric flask. G.l.c. analysis was carried out (Pye 104, 2 m 2½% SGR, 150 °C, R_t 3.7 min) before the contents of the flask were added slowly to refluxing phosphide (0.01 mol) in THF (40 cm^3). The mixture was refluxed for 3 h, cooled and peroxidised in the normal way. Extraction with chloroform and evaporation gave an oil which was diluted to 10 cm^3 with THF in a volumetric flask. G.l.c. showed unchanged biphenylene (87%). The residue was chromatographed (basic alumina); elution with ether gave white crystals of biphenyl-2-yldiphenylphosphine oxide (0.05 g, 3%), m.p. 149—151 °C (Found: C, 81.0; H, 5.0; P, 8.9. Calc. for $C_{24}H_{19}OP$: C, 81.36; H, 5.37; P, 8.76%); $\nu_{max.}$ 1 440, 1 190, 1 145, 1 120, and 1 190 cm^{-1}; *m/z* 354 (M^+) and 277(100%); δ($CDCl_3$) 7.97 (m) and 7.31 (m) (ratio 18 : 26).

1,3-*Diphenylisobenzofuran as a Dehydrobenzene Trapping Agent.*—Lithium diphenylphosphide (0.01 mol) was prepared in THF (25 cm^3). *o*-Dibromobenzene (1.18 g, 0.005 mol) and 1,3-diphenylisobenzofuran (2.98 g, 0.011 mol) in THF (25 cm^3) were added simultaneously and dropwise to the refluxing phosphide solution. The isobenzofuran was shown to contain *ca.* 5% *o*-dibenzoylbenzene (by g.l.c., 2 m 2½% SGR at 240 °C). The reaction mixture was refluxed for 3 h and worked up normally. Chromatography (silica gel) gave *o*-dibenzoylbenzene (1.9 g, 60%), m.p. 147—148 °C (lit.,[20] 148 °C) and traces of 9,10-diphenyl-9,10-epoxyanthracene[21] and 9,10-diphenylanthracene, m.p. 248—250 °C (lit.,[22] 249—250 °C).

Peroxidisation of 1,3-*Diphenylisobenzofuran.*—1,3-Diphenylisobenzofuran (1.35 g, 0.05 mol) was stirred overnight with 6% hydrogen peroxide (50 cm^3). Filtration and chromatography on silica gel gave *o*-dibenzoylbenzene (1.2 g), m.p. 147—148 °C.

Peroxidisation of 9,10-*Diphenylanthracene.*—9,10-Diphenylanthracene (0.83 g, 0.0025 mol) was stirred overnight with 6% hydrogen peroxide (50 cm^3). Extraction with chloroform and evaporation gave a yellow solid which partially decomposed at 135—190 °C and finally melted at 248—250 °C (lit.,[22] m.p. of diphenylanthracene 249—250 °C). Mass spectroscopy and t.l.c. (silica and elution with ether and with light petroleum, b.p. 40—60 °C) showed only diphenylanthracene. G.l.c. retention times were 42.2 min for the starting material and 44.2 min for the reaction product (Pye 104 2 m 2½% SGR, 225 °C).

Reaction of 3,4-*Dichloronitrobenzene with Lithium Diphenylphosphide*.—3,4-Dichloronitrobenzene (3.84 g, 0.02 mol) was added dropwise to a refluxing solution of lithium diphenylphosphide (0.04 mol) in THF (50 cm^3). After the addition was complete refluxing was continued for $\frac{1}{2}$ h and the reaction mixture was cooled and peroxidised. Chromatography of the organic residue on silica gel (pentane) gave 3,3′,4,4′-tetrachloroazobenzene (1.21 g, 38%), m.p. 156—157 °C (lit.,[23] 158 °C) and a dark red oil.

Preparation of o-*Halogenobenzene Diazonium Salts*.—A standard method [24] was employed for the diazotisation of *o*-halogenoanilines to give *o*-bromobenzenediazonium tetrafluoroborate (80%), m.p. 147—148 °C (decomp.) [lit.,[25] 156 °C (decomp.)], *o*-chlorobenzenediazonium tetrafluoroborate (80%), m.p. 167—168 °C (decomp.) [lit.,[25] 171 °C (decomp.)], and *o*-iodobenzenediazonium tetrafluoroborate (71%), m.p. 105—106 °C (decomp.) [lit.,[25] 109 °C (decomp.)].

Reactions of o-*Halogenobenzenediazonium Tetrafluoroborates with Two Equivalents of Lithium Diphenylphosphide in the Presence of Furan*.—The halogenobenzenediazonium tetrafluoroborate (0.01 mol) was added slowly to a solution of lithium diphenylphosphide (0.02 mol) in THF (40 cm^3) and furan (15 cm^3) at 50 °C. Nitrogen was evolved immediately and the red colour darkened. The mixtures were refluxed for 0.5 h, cooled, treated with 6% hydrogen peroxide (50 cm^3), extracted with chloroform and dried ($MgSO_4$). The major products were halogenobenzenes and intractable polymers. The reaction mixtures were analysed by g.l.c. (2 m $2\frac{1}{2}$% SGR at 245 °C) for triphenylphosphine oxide (9.6 min), *o*-chlorophenyldiphenylphosphine oxide (14.5 min), *o*-bromophenyldiphenylphosphine oxide (18.8 min), and *o*-iodophenyldiphenylphosphine oxide (24.0 min), and at 120 °C for 1,4-dihydro-1,4-epoxynaphthalene (6.1 min), chlorobenzene (1.2 min), bromobenzene (1.6 min), and iodobenzene (2.4 min).

o-*Chlorobenzenediazonium tetrafluoroborate*. This compound gave no triphenylphosphine oxide but *o*-chlorophenyldiphenylphosphine oxide (0.3%) and traces of naphthyldiphenylphosphine oxide. No adduct was detected.

o-*Bromobenzenediazonium tetrafluoroborate*. This compound gave triphenylphosphine oxide (0.3%) and a small amount of the adduct (0.5%).

o-*Iodobenzenediazonium tetrafluoroborate*. This compound gave triphenylphosphine oxide (10%) and the furan adduct (1.3%) but no *o*-iodophenyldiphenylphosphine oxide. T.l.c. (silica) showed a major product with an R_F similar to triphenylphosphine oxide. This material could not be crystallised, but showed *m/z* 329.990 97 (M^+) corresponding to a dihydronaphthyldiphenylphosphine oxide.

Lithium Diphenylarsenide.—This reagent was prepared by Aguiar's method [2,26] from triphenylarsine and lithium metal in THF.

Reactions of o-*Dihalogenobenzenes with Lithium Diphenylarsenide in the Presence of Furan*.—The dihalides (0.005 mol) in furan (20 cm^3) were syringed slowly into gently refluxing arsenide (0.01 mol) in THF (50 cm^3). The reaction mixtures were refluxed for 3 h, cooled, transferred to volumetric flasks and diluted (methylene dichloride) to 100 cm^3. Combined g.c.–mass spectrometry of the reaction mixtures showed the presence of diphenylarsine, diphenylarsine oxide, triphenylarsine and, in the reaction of dichlorobenzene, a trace of *o*-chlorophenyldiphenylarsine. Chromatography (silica gel) gave triphenylarsine, m.p. 60 °C (lit.,[27] 60.5 °C), on elution with light petroleum (b.p. 40—60 °C) and ether elution gave the dihalides. G.l.c. (F-17, 2 m $2\frac{1}{2}$% SGR, 235 °C) was used to determine triphenylarsine (10.2 min) and *o*-di-iodobenzene (2.0 min). The yields of triphenylarsine were corrected to take account of uncleaved arsine used to prepare the arsenide. *o*-Dibromo- and *o*-dichloro-benzene were also determined by g.l.c. (104, 2 m, $2\frac{1}{2}$% SGR, 110 °C, R_t 8.2 and 3.4 min, respectively), as was naphthalene (F-17, 2 m $2\frac{1}{2}$% SGR, 150 °C, R_t 3.8 min).

o-*Dichlorobenzene*. This compound gave triphenylarsine (45%) and unchanged dichloride (48%).

o-*Dibromobenzene*. This compound gave triphenylarsine (66%) and unchanged dibromide (13%).

o-*Di-iodobenzene*. This gave triphenylarsine (16%) and unchanged di-iodide (18%). In the absence of furan, *o*-dichlorobenzene gave triphenylarsine (49%) and unchanged dihalide (46%), while *o*-dibromobenzene gave 75 and 21%, respectively.

Reactions of Mixed Halides with Lithium Diphenylarsenide.—The reactions were carried out as for the dihalides above. The amount of triphenylarsine in the original arsenide solution was determined by g.l.c. and the yields from reactions have been corrected to take this into account. Thus the actual ratio of arsenide to dihalide used was 1.84 : 1 instead of 2 : 1. Small amounts of a compound, believed to be $(Ph_2As)_2O$, *m/z* 474, were present in all cases.

Reactions in the Presence of Furan.—o-*Bromofluorobenzene*. This compound gave triphenylarsine (29%), unchanged dihalide (0.5%), and naphthalene (0.1%). Small amounts of o-bromophenyldiphenylarsine [*m/z* 386(1%) and 384(1)] and *o*-fluorophenyldiphenylarsine (*m/z* 324) as well as a trace of naphthyldiphenylarsine (*m/z* 356) were detected by g.c.–mass spectrometry.

o-*Bromochlorobenzene*. This gave triphenylarsine (33%), unchanged halide (32%), and naphthalene (0.4%). *o*-Bromophenyldiphenylarsine and *o*-chlorophenyldiphenylarsine [*m/z* 342(1%), 340(3)] as well as traces of naphthyldiphenylarsine and biphenylyldiphenylarsine (*m/z* 381) were also detected by g.c.–mass spectrometry.

o-*Bromoiodobenzene*. This gave triphenylarsine (14%), dihalide (46%), and naphthalene (1.8%). *o*-Bromophenyl-, naphthyl-, and biphenylyl-arsines were also detected by g.c.–mass spectrometry. No *o*-iodophenyldiphenylarsine was detected.

Reactions in the Absence of Furan.—o-*Bromofluorobenzene*. This gave triphenylarsine (59%), dihalide (20.5%), and *o*-bromo- and *o*-fluoro-phenyldiphenylarsine.

o-*Bromochlorobenzene*. This gave triphenylarsine (43%), dihalide (40%), and *o*-iodo- and *o*-bromo-phenyldiphenylarsine.

Reaction of Lithium Diphenylarsenide and 1,4-*Dihydro*-1,4-*epoxynaphthalene*.—The furan adduct (0.35 g, 0.0025 mol) was added to gently refluxing arsenide (0.005 mol) in THF (20 cm^3). The mixture was refluxed for 3 h, cooled and evaporated. Trituration with light petroleum (b.p. 40—60 °C) gave a brown solid which recrystallised from chloroform–ether to give a compound (0.05 g) [m.p. 280 °C; $\nu_{max.}$ 3 820br and 1 625br cm^{-1}; *m/z* 266(4%), 264(9), 229(9), 228(4), 227(17), 179(3), 177(8), 155(16), 154(100), 153(10), 152(24), 151(17), and 77(17)] which gave a positive lithium flame test and is tentatively identified as lithium diphenylarsinate.

The residue was added to water (100 cm^3) and extracted with chloroform (3 × 150 cm^3). T.l.c. of the extracts (silica gel, ether elution) showed 2 spots, one of which corresponded to naphthalene. G.l.c. (F-17, 2 m $2\frac{1}{2}$% SGR, 220 °C) also showed the presence of naphthalene (1.6 min) and another peak (2.7

min). Both naphthalene and the unknown compound were detected by h.p.l.c. (40% $CHCl_3$–pentane, 0.8 min, 267 nm) with retention times of 1.5 and 5.6 min, respectively.

Chromatography (silica gel) gave (pentane) naphthalene (0.3 g) and a white crystalline compound (40% ether–pentane) (0.05 g), m.p. 42—44 °C, $\nu_{max.}$ (KBr) 2 920, 1 620, 1 580, 1 490, 1 450, 1 340, 1 260, and 735 cm^{-1}. This latter compound was not detected in any of the dihalide reactions with arsenide.

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