Phosphides and Arsenides as Metal–Halogen Exchange Reagents. Part 1. Dehalogenation of Aliphatic Dihalides [1]

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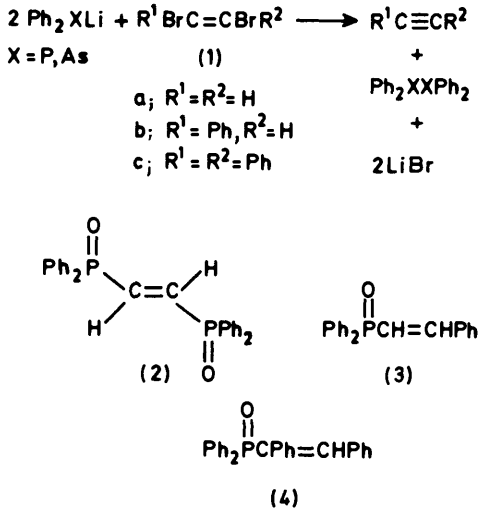
Lithium diphenylphosphide and arsenide have been investigated as reagents for metal–halogen exchange. Reactions involving two molar equivalents of the anions with 1,2-dibromoethylenes lead to moderate to good yields of acetylenes and smaller yields of phosphorus-containing by-products. Similar reactions with 2,3-dichlorobuta-1,3-diene and 2-chlorobuta-1,3-diene give S_N2' rather than direct substitution products. Evidence is presented that adamantene is an initial product in the reaction of lithium diphenylphosphide with 1,2-di-iodo- and 1,2-dibromo-adamantane, but not with 1,2-dichloroadamantane, although 1- and 2-adamantyldiphenylphosphine oxides are formed in every case. Finally reactions of phosphide anion with geminal dihalides were briefly investigated; 1,1-dibromo-2,2-diphenylethylene gave diphenylacetylene as the major product.

Attack on halogen by neutral tervalent phosphorus has been commonly observed and through the work of Appel [2] and Castro [3] has been developed into a series of general synthetic procedures. These compounds have also been used as debrominating reagents.[4] By comparison there have been few reports of attack on halogen by phosphide anions [5] and we are aware of only one example of dehalogenation, that of 1,2-dibromoethane to give ethylene.[6] However, we were encouraged to investigate group 5 anions as metallating, and hence dehalogenating, reagents since organometallic compounds, especially organolithium, have been extensively used in this way [7] and the greater polarisability of group 5 nucleophiles suggests that attack on halogen would be more likely in these cases than for carbon nucleophiles.

Our choice of lithium compounds as reagents was on the basis of greatest polarisability and this is supported by the preferential attack on halogen by lithium phosphides and carbon by sodium phosphides.[6] On the same basis the larger arsenide anion should be a more satisfactory reagent than phosphide.



Results and Discussion

(*a*) *Reactions of* 1,2-*Dihalogenoalkenes.*—Aguiar and his co-workers have extensively investigated the reactions of vicinal vinyl dichlorides with phosphides [8] and have shown that nucleophilic displacement at carbon is the predominant pathway; † however, the softer halogen [5] should encourage attack on bromine in the corresponding dibromide.

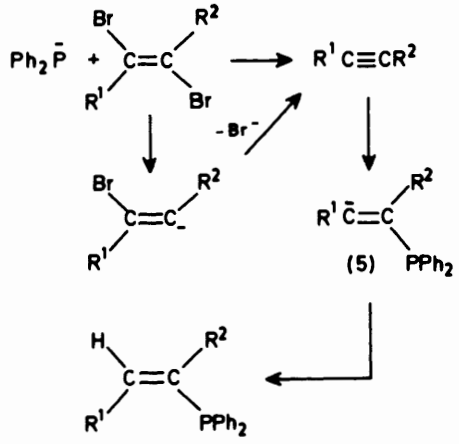
The addition of two molar equivalents of lithium diphenylphosphide or lithium diphenylarsenide to 1,2-dibromoethylene (1a) (64 : 36, *cis* : *trans*), α,β-dibromostyrene (1b) (29 : 71, *cis* : *trans*), and α,β-dibromostilbene (1c) (40 : 60, *cis* : *trans*) in refluxing tetrahydrofuran gave in each case the corresponding acetylene (Table 1). Determination of any preferred stereochemistry for the elimination was precluded by the rapid isomerisation of the dibromides under the reaction conditions.[9] In the phosphide reactions, after oxidative work-up, diphenylphosphinic acid was also formed, while small yields of the oxides (2), (3), and (4) were isolated from reactions with the dibromides (1a), (1b), and (1c), respectively.

The formation of acetylenes in these reactions is presumably *via* initial attack on bromine with concerted or stepwise elimination of bromide (Scheme 1). This is supported by the higher yields of acetylenes obtained from reactions involving two molar equivalents of phosphide or arsenide, since the initially formed bromophosphine or arsine will react rapidly with phosphide or arsenide to give biphosphine (converted into diphenylphosphinic acid on oxidative work-up) or biarsine, and by the recovery of significant amounts of dibromides from reactions involving one molar equivalent of phosphide or arsenide. The lower yields of acetylenes generally obtained from reactions involving arsenides is perhaps surprising since the softer arsenide nucleophile would be expected to show preference for attack on bromine over carbon when compared to phosphide; however, the results may be complicated by the polymerisation of acetylenes in the presence of arsenide.

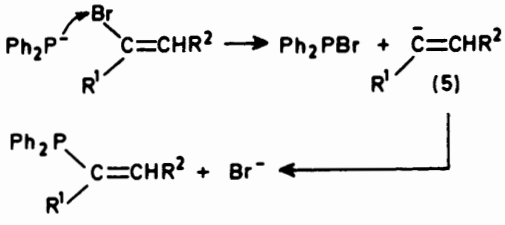
Table 1. Yields of acetylenes from the reactions of 1,2-dibromoethylenes with phosphides and arsenides

$R^1BrC=CBrR^2$			Yield (%) of acetylene			
			Molar ratio of phosphide		Molar ratio of arsenide	
R^1	R^2	% *trans*	1 : 1	2 : 1	1 : 1	2 : 1
H	H	36	50	80	33	46
Ph	H	71	7	37	2	53
Ph	Ph	60	19	33	32	54

† The isolation of biphosphines and biarsines in some cases suggests that attack on halogen also occurs.



Scheme 1.

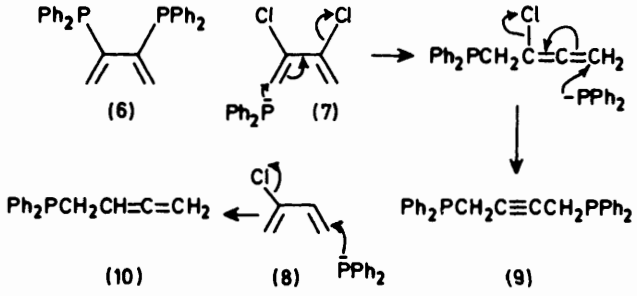


Scheme 2.

The *trans*-1,2-vinylenebis(diphenylphosphine) dioxide (2) formed in the reaction of phosphide with 1,2-dibromoethylene is presumably derived from direct substitution of halide.* It is interesting that the yield of compound (2) is substantially greater in reactions carried out at 0 °C, suggesting that elimination is favoured by increasing the temperature. The formation of similar products from the dibromides (1b) and (1c) is less likely on the basis of (i) increased steric hindrance at carbon, (ii) increased stabilisation of any negative charge build-up, and (iii) increased stabilisation of acetylene-like transition states, by phenyl substituents.

The styryldiphenylphosphine oxide (3) and (β-phenylstyryl)diphenylphosphine oxide (4) isolated from reactions of (1b) and (1c) probably arise from the addition of phosphide to the initially formed acetylene (Scheme 1).[10] However, attempts to confirm the presence of the carbanion (5) in reactions of the dibromides through the addition of D_2O were inconclusive and inverse addition of phosphide to dibromide did not lead to increased yields of acetylenes. The oxides (3) and (4) can also be obtained by reactions of α-bromostyrene [11] and α-bromostilbene with phosphide. Although these reactions are formally simple substitutions at carbon, it seems likely that initial attack of phosphorus is on bromine (Scheme 2).† This latter mechanism can still explain the stereospecificity observed in these substitutions if the intermediate carbanion (5) has configurational stability.[12]

On the basis of these results and the work of Aguiar,[8] the reaction of 2,3-dichlorobuta-1,3-diene (7) with diphenylphosphide might be expected to provide a route to the potentially ambidentate ligand (6). In fact the addition of the dichloride to a solution of lithium diphenylphosphide (2 mol equiv.) in tetrahydrofuran at −70 °C gave a compound which, on the basis of its ^1H and ^{13}C n.m.r. and mass spectra, was identified as 1,4-bis(diphenylphosphinyl)but-2-yne (9). This structure was confirmed by synthesis from lithium diphenylphosphide and 1,4-dichlorobut-2-yne.[13] No evidence for attack on halogen was observed and the formation of the alkyne (9) can be rationalised by two S_N2'-type reactions with phosphide anion (Scheme 3). Support for this mechanism is provided by a similar reaction of diphenylphosphide anion with chloroprene (2-chlorobuta-1,3-diene) to give allenyldiphenylphosphine (10); the site for phosphide attack is presumably controlled by steric effects [14] in both cases. Similar reactions of compounds (7) and (8) with diphenylarsenide gave analogous products, but in low yield.



Scheme 3.

Under certain conditions the reaction of diphenylphosphide with 3-chloropropyne gives products (11) and (12) [5] [equation (1)] which could be explained by a similar initial attack on acetylenic carbon. However, the authors have conclusively

$$Ph_2P^- + ClCH_2C{\equiv}CH \xrightarrow{THF} \underset{(11)}{Ph_2PCH{=}C{=}CH_2} + \underset{(12)}{Ph_2PC{\equiv}CCH_3} \quad (1)$$

shown that the reaction involves substitution at saturated carbon followed by base-catalysed prototropic rearrangements. The nature of the products excludes this type of pathway for the reactions of chlorobutadienes with phosphide.

(*b*) *Reactions with* 1,2-*Dihalogenoadamantanes.*—A range of methods have been used to generate cycloalkenes where ring-strain precludes effective overlap between the p-orbitals forming the π-bond.[15] Adamantene (13) has proved especially elusive since the generally used Hofmann elimination route failed. In dehalogenation reactions using butyl-lithium, only iodides (14) and (15) provided any evidence for the adamantene intermediate,[16] although debromination of 1,2-dibromoadamantane with bis(trimethylsilyl)mercury [17] was successful.‡

The addition of 1,2-di-iodoadamantane to a refluxing solution of lithium diphenylphosphide in tetrahydrofuran, followed by oxidative work-up, gave adamantene dimer (18) (identified by g.l.c. comparison with an authentic sample [16b]), 1-adamantyldiphenylphosphine oxide (16) and 2-adamantyldiphenylphosphine oxide (17), which were identical (i.r., n.m.r., m.p. and mixed m.p.) with authentic samples prepared by the reaction of phosphide with 1- and 2-bromoadamantane followed by oxidation. G.l.c. and h.p.l.c. also showed the presence of a so far unidentified compound, which was shown

* The *trans* stereochemistry of (2) may indicate that a *syn* elimination pathway is preferred since the formation of (2) from a similar reaction of 1,2-dichloroethylene is reported to be stereospecific.[8]

† This may not be the case for reactions in the presence of amines,[10] where the phosphide is thought to be much more ionic owing to co-ordination of the lithium cation by amine.

‡ We thank a referee for drawing our attention to this paper.

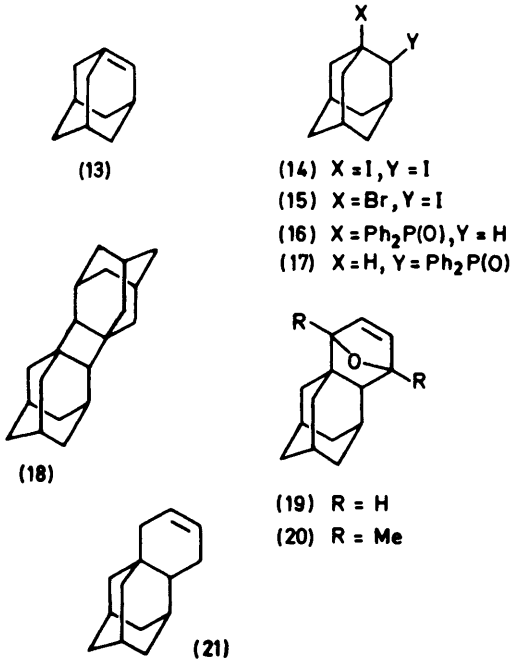


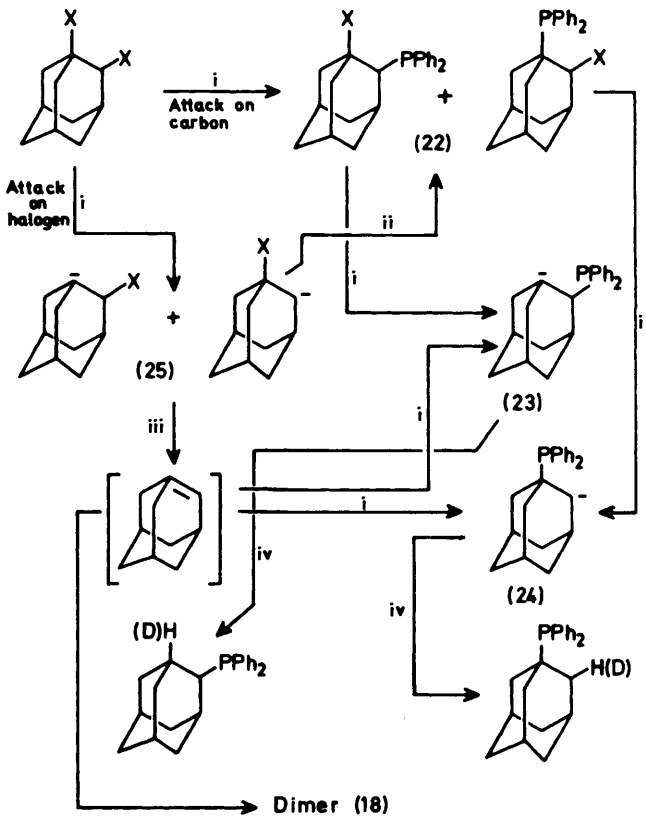
Table 2. Yields of products from the reaction of 1,2-dihalogenoadamantanes with lithium diphenylphosphide after oxidation

Halide	Dimer (%)	Yield of 1- and 2-adamantylphosphine oxides (%) 1-	2-	Unidentified isomer	Unchanged dihalide (%)
Cl	0	0.2	0.8	0	2
Br	5	7.4	3.7	8	4
I	4	10	5	14	4

by combined g.l.c.–mass spectroscopy to be isomeric with the adamantylphosphine oxides. An analogous reaction with 1,2-dibromoadamantane gave similar results, but reaction with 1,2-dichloroadamantane gave trace amounts of 1- and 2-adamantyldiphenylphosphine oxides and 1-chloroadamantane as the only identified products. In no case did the yield of unchanged 1,2-dihalogenoadamantane exceed 4%. These results are summarised in Table 2.

Similar reactions in the presence of furan or 2,5-dimethylfuran gave the same products and no trace of the adducts (19) or (20).[18] However, g.l.c. of a reaction carried out at 0 °C for two days in the presence of butadiene showed the presence of the adamantene adduct (21).[16b]

Scheme 4 summarises possible mechanisms of formation for the observed products. The isolation of the dimer (18) and the adduct (21) from reactions with 1,2-dibromo- and 1,2-diiodo-adamantane strongly supports the involvement of an adamantene intermediate. That the formation of 1- and 2-adamantyldiphenylphosphine oxides also involves adamantene in these cases is indicated by both the similar product ratio of 1- to 2-oxides in each case and by its absolute value, since on the basis of carbanion stability an adamantene route should give 1-adamantyldiphenylphosphine oxide as the major isomer (in spite of Hammond's postulate,[19] all known nucleophilic additions to strained alkenes are regioselective in a Markovnikov manner [20]). A preference for the opposite mode of addition would be predicted for the route *via* the halogenoadamantyldiphenylphosphines (22) and this *is* observed in the



Scheme 4. *Reagents:* i, Ph_2P^-; ii, PhPX; iii, $-X^-$; iv, H_2O (D_2O)

reaction with 1,2-dichloroadamantane * which, together with the absence of dimer (18) from this reaction, suggests a mechanism *via* the diphenylphosphine compound (22; X = Cl).

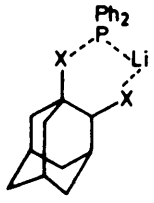
Although deuteriation studies do not distinguish between the alternative pathways, they do implicate anions (23) and (24) as intermediates since both 1- and 2-adamantyldiphenylphosphine oxides obtained from experiments quenched with D_2O were >80% monodeuteriated.

The detailed mechanism of adamantene formation from the adamantyl anions (25) is still obscure since these intermediates face the problem of non-alignment of the lone-pair orbital and the bond to the leaving group. In view of the tendency for alkyl-lithiums to exist as aggregates in solution [21] it is significant that adamantene does not appear to be an intermediate in experiments with sodium diphenylphosphide; a species such as (26) would presumably assist the halide leaving group and an analogous transient species has been suggested [22] in reactions of phosphides with halogenobenzenes.†

(*c*) *Reactions with Geminal Dihalides.*—1,1-Dibromo-2,2-diphenylethylene reacts with lithium diphenylphosphide (2 mol equiv.) in refluxing tetrahydrofuran to give, after oxidative work-up, diphenylacetylene, (2,2-diphenylvinyl)diphenylphosphine oxide (29) and an unidentified orange oil (Scheme 5). 1,1-Dihalogeno-2,2-diarylethylenes are reported

* We have been unable to observe the presence of any adduct (21) from such experiments in the presence of butadiene.

† Recently reported ^{31}P and ^{7}Li n.m.r. studies show that lithium diphenylphosphide is covalent and dimeric in diethyl ether at low temperatures (I. J. Colquhoun, H. C. E. McFarlane, and W. McFarlane, *J. Chem. Soc., Chem. Commun.*, 1982, 220).



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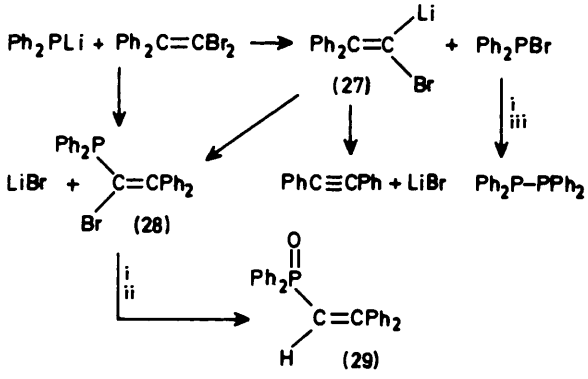
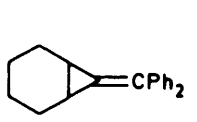


Scheme 5. *Reagents:* i, Ph_2PLi; ii, H_2O/H_2O_2; iii, $-LiBr$

to form diarylacetylenes on reaction with organolithium reagents [23] and the reaction is thought to involve initial metallation to give compound (27) followed by aryl migration. Carbene involvement has been discounted in these reactions on the grounds that no addition to added alkenes could be observed; [24] reaction of 1,1-dibromo-2,2-diphenylethylene with lithium diphenylphosphide in the presence of cyclohexene offered evidence (g.c.–mass spectrum) of only traces of the adduct (30).

The formation of the oxide (29) could be explained by phosphide attack on bromine in the intermediate phosphine (28); however, deuterium incorporation into (29) was not observed when the reaction mixture was quenched with D_2O before oxidation.

Reactions of 7,7-dichloro- and 7,7-dibromo-norcarane with lithium diphenylphosphide gave complex mixtures of products (>30 by g.l.c.); however, the major product in each case was a phosphine oxide, tentatively identified as 7-norcaryldiphenylphosphine oxide (31).



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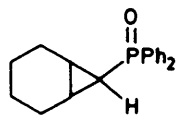

(31)

Experimental

M.p.s were determined on a Kofler block and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer Grating Infracord spectrophotometer 457. N.m.r. spectra were obtained on a Varian HA60 and a Bruker WH90 spectrometer. G.l.c. analysis was performed on a Perkin-Elmer F-11 or F-17 and on a Pye 104 instrument. Preparative g.l.c. was carried out on a Perkin-Elmer F-21 chromatograph. Mass spectra were recorded on an A.E.I. MS902 mass spectrometer. Combined g.l.c.–mass spectra were carried out on a Pye 104 g.l.c. coupled to an A.E.I. MS30 mass spectrometer. High pressure liquid chromatography was performed on a Spectra-Physics 3500 model employing a 3 mm × 250 mm column packed with 5μ spheresorb silica. A typical flow rate was 1.2 cm^3/min using a mixture of chloroform–pentane (40 : 60). H.p.l.c. detection was by u.v. absorption on a Cecil CE212 variable wavelength u.v. monitor. All experiments involving phosphines and other readily oxidised materials were carried out under an atmosphere of dry, oxygen-free, nitrogen. Tetrahydrofuran (THF) used in reactions was dried over calcium chloride, then over sodium wire and finally freshly distilled from lithium aluminium hydride. Ether refers to diethyl ether throughout.

Lithium Diphenylphosphide.—This compound was prepared by Issleib's method.[25] Diphenylphosphine (1.86 g, 0.01 mol) was syringed into dry THF (50 cm^3) under nitrogen in a three-necked flask connected to a gas burette. n-Butyllithium (0.64 g, 0.01 mol) in hexane was added, giving a deep red solution. This solution was refluxed for ½ h and the gas evolved measured (220 cm^3 = 100%).

cis,trans-1,2-*Dibromoethene.*—This compound was obtained commercially (Ralph N. Emmanuel). An attempt to prepare the pure *cis* isomer by selective debromination of the *trans* form using zinc and zinc chloride was unsuccessful. Distillation on a spinning band [polyfluorotetraethylene (PTFA)] column gave mixtures whose composition ranged from 30—90% *trans*. When the mixtures were heated at 50 °C in THF for ½ h the equilibrium value was re-established at *cis* : *trans* 64 : 36 (by n.m.r.; vinyl protons at δ 6.93 for *cis* and 7.32 for *trans*).

cis,trans-α,β-*Dibromostyrene.*—The procedures of König and Wolf [26] were followed to prepare pure *cis*, pure *trans*, and an isomeric mixture of dibromostyrenes from phenylacetylene. Chromatography (silica gel) of the *cis* : *trans* mixture gave (on eluting with pentane) fractions with the percentage of *cis* isomer increasing from 29—88%. When *cis*-dibromostyrene (2 cm^3) was heated in THF (25 cm^3) at 50 °C for 1 h, the equilibrium mixture (*cis* : *trans* 29 : 71) was attained (vinyl protons, *cis* δ 6.98, *trans* δ 6.75).

cis,trans-α,β-*Dibromostilbene.*—This compound was prepared by the dropwise addition of bromine (1.4 cm^3) to diphenylacetylene (4 g) in glacial acetic acid (50 cm^3) at room temperature. The mixture was stirred for 1 h and filtered. The dibromide was washed with methanol to give white crystals (80%), m.p. 204—211 °C (lit.,[27] 205—206 °C).

Reactions of Lithium Diphenylphosphide with 1,2-*Dibromoolefins.*—Lithium diphenylphosphide was prepared (0.01 mol) in THF as previously described. The dibromide was added, dropwise, neat if a liquid or in a minimum of THF if a solid. The resulting solution was refluxed for 1 h under nitrogen, cooled, treated with excess of 6% hydrogen peroxide, extracted with chloroform, dried and evaporated. The residue was made up to a known volume with methylene dichloride for g.l.c. analysis.

1,2-*Dibromoethene.* Acetylene was detected by bubbling the evolved gas through ammoniacal cuprous chloride (25 g in 600 cm^3), in which red cuprous acetylide was formed.[28] Yields of acetylene were determined by displacement of water. Phosphide (2 equiv.) gave acetylene (80%) and traces of *trans*-1,2-vinylenebis(diphenylphosphine) dioxide (by mass spectroscopy) (1 equiv. yielded 50% acetylene).

1,2-*Dibromoethene and lithium diphenylphosphide at* 0 °C. The phosphide (1 equiv.) was prepared and cooled in an ice–salt bath. Dibromide was added so as to maintain the

temperature at 0 ± 1 °C. Acetylene (23%) was collected. Trituration of the residue gave diphenylphosphinic acid (0.25 g, 8%), m.p. 195 °C (lit.,[29] 195—196 °C). The acetone extract was evaporated and the residue crystallised from chloroform to give *trans*-1,2-vinylenebis(diphenylphosphine) dioxide (0.83 g, 19%), m.p. 304 °C (lit.,[8] 304 °C).

Attempted deuterium incorporation. Deuterium oxide (10 cm³) was added to the reaction mixture obtained at 0 °C. The normal work-up gave *trans*-1,2-vinylenebis(diphenylphosphine) dioxide, *m/z* 428 (no incorporation).

cis,trans-α,β-*Dibromostyrene.* Lithium diphenylphosphide (0.02 mol) and dibromostyrene (2.62 g, 0.01 mol) gave phenylacetylene (37%) by g.l.c. (F-11, 70 °C, 2 m 2½% SGR). The reaction mixture was chromatographed (silica gel). Elution with light petroleum (b.p. 40—60 °C)–ether (9 : 1) gave a trace of dibromide. Ether elution gave phenylacetylene. Ethyl acetate gave styryldiphenylphosphine oxide (0.27 g), m.p. 165—166 °C (Found: C, 78.95; H, 5.65. Calc. for $C_{20}H_{17}OP$: C, 78.94; H, 5.91%). The i.r., n.m.r., and mass spectra were consistent with those of *trans*-β-styryldiphenylphosphine oxide.[11] Phosphide (1 equiv.) gave phenylacetylene (7%).

Inverse addition. The phosphide was prepared as usual and added slowly, under nitrogen, to a refluxing THF solution of dibromostyrene (1 equiv.). Work-up in the usual manner gave phenylacetylene (5%).

cis,trans-α,β-*Dibromostilbene.* Phosphide (2 equiv.) gave diphenylacetylene (33%) and unchanged dibromide (9%) by g.l.c. (F-11, 2 m 2½% SGR, 190 °C). Chromatography on silica gel gave these two compounds on elution with ether and with ethyl acetate, and an oily residue, $\nu_{max.}$ (KBr) 1 440, 1 175, and 1 110 cm⁻¹; *m/z* 381(28%), 380(100), 379(67), 378(29), 377(40), and 178(39), which could not be crystallised but which was spectroscopically identical (i.r., mass spectrum) with a sample of *cis*-1,2-diphenylvinyldiphenylphosphine oxide prepared by Aguiar's method from diphenylacetylene and lithium diphenylphosphide in the presence of diethylamine.[10] A similar reaction with phosphide (1 equiv.) gave diphenylacetylene (19%) (g.l.c. as above). In this, as in all phosphide experiments, diphenylphosphinic acid was isolated, m.p. 193—195 C (lit.,[29] 195—196 °C).

trans-1,2-*Vinylenebis(diphenylphosphine) Dioxide.*—This compound was prepared from *trans*-1,2-dichloroethene and lithium diphenylphosphide by Aguiar's method.[8]

trans-*Styryldiphenylphosphine Oxide.*—This compound was prepared by Aguiar's route [11] from β-bromostyrene.

Reaction of Phenylacetylene with Lithium Diphenylphosphide.—Phenylacetylene (1.02 g, 0.01 mol) was added, dropwise, to refluxing lithium diphenylphosphide (0.1 mol) in THF (50 cm³). The mixture was heated for 6 h and worked up as usual. 2-Styryldiphenylphosphine oxide (60%), m.p. 165—166 °C, was obtained. The i.r. and n.m.r. were as reported for the *trans* isomer.[11]

Lithium Diphenylarsenide.—This compound was prepared by Aguiair's method [30] from triphenylarsine (30.6 g, 0.1 mol) and lithium metal (1.4 g, 0.2 mol) in THF. The yellow-red solution was then transferred to a volumetric flask, diluted to 100 cm³ with THF, and used within 12 h to obtain consistent results.

Reactions of Lithium Diphenylarsenide with Dibromoolefins.—A portion (10 cm³, 0.01 mol) of the stock solution of lithium diphenylarsenide was syringed into THF (40 cm³) under nitrogen and heated until the solution was gently refluxing. The dibromide (0.01 mol or 0.005 mol) was slowly added neat, or if a solid in a minimum of THF, to the arsenide. The solution was heated for 1 h, poured into water (100 cm³) and extracted with chloroform (3 × 10 cm³). The extracts were dried, evaporated and made up to 100 cm³ with methylene dichloride for g.l.c. analysis (conditions as for phosphide experiments above).

1,2-*Dibromoethylene.* This compound, with arsenide (2 equiv.), gave acetylene (46% by gas burette) while 1 equiv. gave 33%.

α,β-*Dibromostyrene.* This compound, with arsenide (2 equiv.), gave phenylacetylene (53%) while only 2% was obtained using equimolar quantities.

α,β-*Dibromostilbene.* This compound, with arsenide (1 equiv.), gave diphenylacetylene (32%) and unchanged dibromide (64%). With 2 equiv., 54% of diphenylacetylene was obtained. Chromatography on silica gel gave diphenylacetylene (ether–pentane 5 : 95) and triphenylarsine (0.15 g), m.p. 60 °C (lit.,[31] 60.5 °C). Further elution with methanol–ether (10 : 90) gave a thick oil (0.54 g) which was shown to contain benzyldiphenylarsine; $\nu_{max.}$ (KBr) 1 785br, 1 430, 1 085, 900, 875, 845, 790, 775, 750, and 690 cm⁻¹; *m/z* 321(28%), 320(100), 227(90), and 152(80).

Reactions of Lithium Diphenylphosphide with 2-Chlorobutadienes.—2,3-Dichlorobuta-1,3-diene (0.1 mol) in THF (10 cm³) was added to a solution of phosphide (0.02 mol) in THF (10 cm³) at −70 °C during ½ h and the reaction mixture stirred overnight at room temperature. Evaporation gave an oil which could be crystallised from benzene–ethanol to give 1,4-bis(diphenylphosphinyl)but-2-yne (64%), m.p. 78—80 °C; *m/z* 422 (M^+); δ($CDCl_3$) 2.87 (4 H, b t, J_{PCH} 3.5 Hz, J_{PCCCH} 2.6 Hz), and 7.7—7.9 (20 H, m); δ(¹³C) ($CDCl_3$) 18.65 (d, $^{13}CH_2$, J_{PC} 17.7 Hz), 78.0 (t, $^{13}C{\equiv}C$), and 128.2—133.0 p.p.m. (m, aromatics). A spectroscopically identical sample was prepared by the reaction of 1,4-dichlorobut-2-yne and lithium diphenylphosphide.[13]

A similar reaction with 2-chlorobuta-1,3-diene gave allenyldiphenylphosphine (62%), m.p. 180—183 °C; $\nu_{max.}$ (KBr) 1 960 and 1 438 cm⁻¹; δ($CDCl_3$) 2.90 (2 H, dt, J_{PCH} 8.8 Hz, J_{HH} 2.6 Hz), 4.80 (2 H, m), 5.36 (1 H, m), and 7.6—7.8 (10 H, m); δ(¹³C) ($CDCl_3$) 23.78 (d, $^{13}CH_2$, J_{PC} 14.7 Hz), 70.97 (s, $^{13}CH_2{=}$), 81.39 (d, $^{13}CH{=}$, J_{PCC} 10.3 Hz), 123.9 (m, Ph), and 128.0 (m, Ph), which on oxidation with hydrogen peroxide (6%) gave the corresponding phosphine oxide, m.p. 208—210 °C; $\nu_{max.}$ (KBr) 1 938 and 1 190 cm⁻¹; *m/z* 254 (M^+) (Found: C, 75.8; H, 5.65; P, 12.0. Calc. for $C_{16}H_{15}OP$: C, 75.59; H, 5.90; P, 12.20%).

Similar reactions of 2,3-dichlorobuta-1,3-diene and 2-chlorobuta-1,3-diene with lithium diphenylarsenide gave 1,4-bis(diphenylarsenyl)but-2-yne and allenyldiphenylarsine.

1,2-*Dihalogenoadamantanes.*—McKervey's route [32] to 1,2-dihalogenoadamantanes from protoadamantan-4-one was employed to prepare 1,2-dichloro-, 1,2-dibromo-, and 1,2-di-iodo-adamantane.

Reactions of 1,2-Dihalogenoadamantanes with Lithium Diphenylphosphide.—The dihalides (0.001 mol) in THF (5 cm³) were added slowly to a refluxing solution of phosphide (0.002 mol) in THF (10 cm³). The reaction mixtures were heated at reflux for 2 h and then treated with hydrogen peroxide (100 cm³) overnight. The products were extracted (chloroform), dried ($MgSO_4$), evaporated and made up to 100 cm³ with methylene dichloride. Adamantene dimer was identified by g.l.c. comparison with authentic dimer (2-CEMS, SGR, and silicone grease columns). The yields of 1- and 2-adamantyldiphenylphosphine oxides were determined by g.l.c. (F-17, 2 m 2½% SGR at 240 °C). Retention times were

28.4 and 20.9 min respectively. The reaction mixtures showed a third peak (26.4 min) which was shown by its g.c.–mass spectrum to have the same molecular ion. The yields given for this third compound are based on it having the same response as 1-adamantyldiphenylphosphine oxide. Traces of a compound corresponding to biadamantyldiphenylphosphine oxide were also detected (*m/z* 470).

1,2-*Dichloroadamantane*. This compound gave unchanged dichloride (2%), 1-adamantyldiphenylphosphine oxide (0.8%), and 2-adamantyldiphenylphosphine oxide (0.2%).

1,2-*Dibromoadamantane*. This compound gave dibromide (4%), dimer (5%), 1-adamantyldiphenylphosphine oxide (7.4%), 2-adamantyldiphenylphosphine oxide (4%), and an isomer (8%).

1,2-*Di-iodoadamantane*. This compound gave dimer (4%), 1-adamantyldiphenylphosphine oxide (10%), 2-adamantyldiphenylphosphine oxide (5%), and an isomer (14%).

Preparation of 1-*Adamantyldiphenylphosphine Oxide*.—1-Bromoadamantane (0.005 mol) was added slowly to a refluxing phosphide solution (0.025 mol) in THF (40 cm^3) and refluxed for 1 h. After the normal oxidative work-up, a yellow oil was obtained and chromatographed (basic alumina). Elution with ethyl acetate gave 1-adamantyldiphenylphosphine oxide (1.1 g, 65%), m.p. 219—222 °C (light petroleum, b.p. 80—100 °C), $\nu_{max.}$ (KBr) 3 040, 2 320, 1 200, and 1 130 cm^{-1}; *m/z* 337(6%), 336(24), 202(72), 201(100), and 135(68); δ($CDCl_3$) 7.91 (m), 7.18 (m), 1.97 (s), 1.89 (s), and 1.78 (s) (ratio of aromatic to aliphatic hydrogens 1 : 1.51) (Found: C, 78.5; H, 7.5; P, 9.0. Calc. for $C_{22}H_{25}OP$: C, 78.54; H, 7.49; P, 9.21%).

Preparation of 2-*Adamantyldiphenylphosphine Oxide*.—2-Bromoadamantane [33] (1.12 g, 0.0052 mol) was added slowly to refluxing phosphide (0.01 mol) and the procedure for the 1-adamantyldiphenylphosphine oxide was followed. Chromatography (as before) gave 2-adamantyldiphenylphosphine oxide (1.3 g, 75%), m.p. 209—211 °C (light petroleum, b.p. 80—100 °C) (Found: C, 78.6; H, 7.65; P, 9.25. Calc. for $C_{22}H_{25}OP$: C, 78.54; H, 7.49; P, 9.21%); $\nu_{max.}$ (KBr) 2 900, 1 480, and 1 180 cm^{-1}; *m/z* 336(40%), 335(78), 202(100), and 201(65).

Reaction of 1,1-*Dibromo*-2,2-*diphenylethene with Lithium Diphenylphosphide*.—1,1-Dibromo-2,2-diphenylethylene was prepared by the published method [34] from tribromoacetaldehyde. The dibromide (0.34 g, 0.001 mol) was added slowly to a refluxing solution of lithium diphenylphosphide (0.002 mol) in THF (20 cm^3). The mixture was refluxed for 3 h, cooled, peroxidised, extracted, and dried in the normal manner. G.l.c. analysis (2½% SGR, 200 °C) showed the presence of diphenylacetylene (16%), which was isolated by chromatography (silica gel) on elution with ether–light petroleum (50 : 50). Elution with ether gave an unidentified orange liquid (0.7 g). Further elution with ether gave 1,1-diphenyl-2-diphenylphosphinylethene oxide (0.068 g, 18%), m.p. 224—226 °C (ethyl acetate–pentane) (Found: C, 81.65; H, 5.75. Calc. for $C_{26}H_{21}OP$: C, 82.09; H, 5.56%), $\nu_{max.}$ (KBr) 1 590, 1 430, 1180, and 1 110 cm^{-1}; *m/z* 380(1.5%), 379(5.5), 201(100), 182(20), and 124(38); δ($CDCl_3$) 1.1 (1 H, d) and 6.9—7.9 (20 H, m).

When the reaction was carried out in cyclohexene (10 cm^3), a trace of a compound *m/z* 260 was detected (g.c.–mass spectrum), but the major product was an intractable oil which g.c. showed to contain diphenylacetylene (3%).

Attempted deuterium incorporation. When the reaction mixture was treated with deuterium oxide (10 cm^3) before the addition of hydrogen peroxide and then worked up in the usual way the 1,1-diphenyl-2-diphenylphosphinylethene oxide isolated showed no deuterium incorporation [*m/z* 380(17%) and 379(5.6)].

7,7-*Dibromo- and* 7,7-*Dichloro-bicyclo*[4.1.0]*heptanes*.—These compounds were prepared by the method of Doering and Hoffman [35] from cyclohexene and bromoform and chloroform, respectively.

Reactions of Dihalogenobicyclo[4.1.0]*heptanes with Lithium Diphenylphosphide*.—The phosphide (0.02 mol) was prepared in the usual manner and the dihalide (0.01 mol) added slowly to the refluxing solution. After 3 h at reflux, the solution was cooled, peroxidised and extracted as before., G.l.c. retention times observed were (F-17, 1 m 2½% SGR, 150 °C) 12.0, 9.8, 8.7, 6.2, and 3.6 min (these peaks were also observed in the products of the reaction between the dibromide and butyllithium) and 5.4, 2.8, 2.6, and 3.6 min. At 240 °C on the same column, a further 10 major peaks were observed at 40.6, 30.2, 26.0, 22.2, 9.3, 8.2, 6.0, 3.6, 2.8, and 1.8 min. The reaction mixtures were distilled and fractions collected up to 80 °C and between 80 and 120 °C. An attempt was made to separate the more volatile components by preparative g.l.c. (Perkin-Elmer F-21, 5 m, 20% Carbowax) but this was unsuccessful. The product from the dichloride reaction was chromatographed (silica gel). Good separation was not obtained although fractions were obtained enriched with the major component (g.l.c. 240 °C R_t 26.0 min) on elution with ethyl acetate. These fractions were further purified by preparative t.l.c. (silica gel on elution with ethyl acetate) to give a sample of norcaryldiphenylphosphine oxide, m.p. 162—171 °C (light petroleum b.p. 60—80 °C) of unknown stereochemistry but only one peak was obtained on g.l.c. This sample was used as a g.l.c. standard to determine the yields of phosphine oxide. Thus dichloronorcarane gave, on reaction with lithium diphenylphosphide (2 equiv.), norcaryldiphenylphosphine oxide (41%), while the dibromide gave 32%. No dihalide remained in either case.

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References

1 Part of this work has been the subject of preliminary publication; D. G. Gillespie and B. J. Walker, *Tetrahedron Lett.*, 1975, 4709; *ibid.*, 1977, 1673; M. Arthurs, S. M. Nelson, and B. J. Walker, *Tetrahedron Lett.*, 1978, 1153.

2 *E.g.* R. Appel and M. Halstenberg, 'Organophosphorus Reagents in Organic Synthesis,' ed. J. I. G. Cadogan, Academic Press, London, 1979, p. 387.

3 *E.g.* Y. Chapleur, B. Castro, and B. Gross, *Tetrahedron*, 1977, **33**, 1615.

4 *E.g.* C. J. Devlin and B. J. Walker, *J. Chem. Soc., Perkin Trans. 1*, 1972, 1249 and references therein.

5 W. Hewertson and I. C. Taylor, *Chem. Commun.*, 1970, 119; W. Hewertson, I. C. Taylor, and S. Trippett, *J. Chem. Soc. C*, 1970, 1835.

6 K. Issleib and D. W. Muller, *Chem. Ber.*, 1959, **92**, 3175.

7 For examples see 'The Chemistry of Organolithium Compounds,' B. J. Wakefield, Pergamon, Oxford, 1974.

8 A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, 1964, **86**, 2299; A. M. Aguiar, J. T. Mague, H. J. Aguiar, T. G. Archibald, and G. Prejean, *J. Org. Chem.*, 1968, **33**, 1681.

9 It has been suggested that phosphines, being ' soft,' two electron nucleophiles, probably give only *anti*-elimination; I. J. Borowitz, D. Weiss, and R. K. Crouch, *J. Org. Chem.*, 1971, **36**, 2377.
10 A. M. Aguiar and T. G. Archibald, *Tetrahedron Lett.*, 1966, 5541; A. M. Aguiar, T. G. Archibald, and L. A. Kapicak, *Tetrahedron Lett.*, 1967, 4447.
11 A. M. Aguiar and D. Daigle, *J. Org. Chem.*, 1965, **30**, 3527; *ibid.*, 2826.
12 D. Y. Curtin and E. E. Harris, *J. Am. Chem. Soc.*, 1951, **73**, 2716; *ibid.*, 4519; D. Y. Curtin, H. W. Johnson, and E. C. Steiner, *J. Am. Chem. Soc.*, 1955, **77**, 4566.
13 R. B. King and A. Efraty, *Inorg. Chim. Acta*, 1970, **4**, 123.
14 A. M. Aguiar and D. Daigle, *J. Am. Chem. Soc.*, 1964, **86**, 2299; S. Chan, H. Goldwhite, H. Keyser, D. G. Roswell, and R. Tang, *Tetrahedron*, 1969, **25**, 1097.
15 R. Keese, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 528; J. F. Liebman and A. Greenberg, *Chem. Rev.*, 1976, **76**, 311; G. L. Buchanan, *Chem. Soc. Rev.*, 1974, **41**, 3.
16 (*a*) D. Lenoir and J. Firl, *Annalen*, 1974, 1467; (*b*) W. Burns, D. Grant, M. A. McKervey, and G. Step, *J. Chem. Soc. C*, 1976, 234.
17 J. I. G. Cadogan and R. Leardini, *J. Chem. Soc., Chem. Commun.*, 1979, 783.
18 H. J. Alberts, H. Strating, and H. Wynberg, *Tetrahedron Lett.*, 1973, 3047.
19 G. S. Hammond, *J. Am. Chem. Soc.*, 1955, **77**, 334.
20 J. E. Gano and L. Eizenburg, *J. Am. Chem. Soc.*, 1973, **95**, 972; J. R. Wisenman and W. A. Fletcher, *J. Am. Chem. Soc.*, 1970, **92**, 956; J. A. Marshall and H. Faubel, *J. Am. Chem. Soc.*, 1970, **92**, 948.
21 W. Tochtermann, *Angew. Chem., Int. Ed. Engl.*, 1966, **5**, 351.
22 A. M. Aguiar, H. J. Greenberg, and K. E. Rubenstein, *J. Org. Chem.*, 1963, **28**, 2091.
23 G. Kobrich, H. R. Merkle, and H. Trappe, *Tetrahedron Lett.*, 1965, 969.
24 G. Kobrich, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 49.
25 K. Issleib and D. Jacob, *Chem. Ber.*, 1961, **94**, 107.
26 J. Konig and V. Wolf, *Tetrahedron Lett.*, 1970, 1629.
27 H. Suzuki, *Bull. Chem. Soc. Jpn.*, 1960, **33**, 396.
28 A. I. Vogel in ' Practical Organic Chemistry,' Longmans, London, 1966, p. 245.
29 G. M. Kosolapoff and R. F. Struck, *J. Chem. Soc.*, 1959, 3950.
30 A. M. Aguiar and T. G. Archibald, *J. Org. Chem.*, 1967, **32**, 2627.
31 R. L. Shrimer and C. N. Wolf, *Org. Synth.*, 1950, **30**, 96.
32 B. D. Cuddy, D. Grant, and M. A. McKervey, *J. Chem. Soc. C*, 1971, 3174.
33 A. C. Udding, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 1968, 1345.
34 H. Goldschmidt, *Chem. Ber.*, 1973, **106**, 985.
35 W. Von E. Doering and A. K. Hoffman, *J. Am. Chem. Soc.*, 1954, **76**, 6162.

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