

REACTIONS OF METAL PHOSPHIDES AND ARSENIDES.

S_N2' PRODUCTS FROM 2-CHLOROBUTADIENES.

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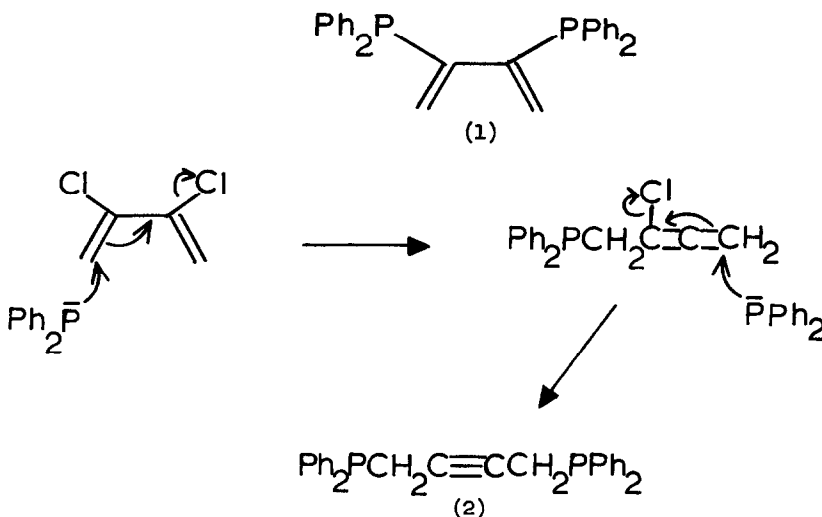
Phosphide anions react with vicinal dihalides in several different ways. Both saturated and vinyl dihalides can undergo attack on carbon² (resulting in substitution) or attack on halogen³ (resulting in elimination and possibly substitution) depending on the nature of the halogen atom.

In view of this we predicted that the reaction of diphenylphosphide anion with 2,3-dichlorobuta-1,3-diene should give the potentially ambidentate ligand (1). In fact the addition of the dichloride to a solution of two molar equivalents of lithium diphenylphosphide in THF at -70° over 30 minutes, followed by stirring overnight at room temperature, gave an oil which could be crystallized from benzene-ethanol to give a compound, m.p. $78-80^\circ$; m/e 422 (M^+); 1H n.m.r.

δ ($CDCl_3$) 2.87 (4H, bt, $J_{PCH} = 3.5$ Hz, $J_{PCCCH} = 2.6$ Hz) and 7.7-7.9 (20H, m); ^{13}C n.m.r.

δ (p.p.m. from TMS; $CDCl_3$) 18.65 (d, $^{13}CH_2$, $J_{PC} = 17.7$ Hz), 78.0 (t, $^{13}C\equiv C$) and 128.2-133.0 (m, Ph). These data suggest a biphosphine acetylene structure (2) and this was confirmed by comparison with an authentic sample prepared by the reaction of diphenylphosphide with 1,4-dichlorobut-2-yne.⁴

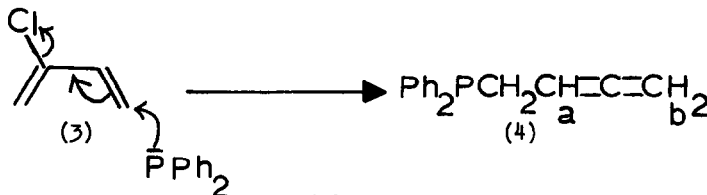
No evidence for attack on halogen was observed³ and the formation of (2) can be rationalised by two S_N2' -type reactions with phosphide anion (see scheme I). Support for this mechanism was



Scheme I

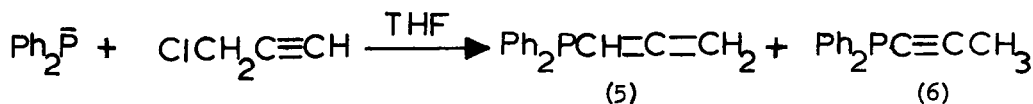
provided by a similar reaction of diphenylphosphide anion with chloroprene (3) to give allenyl-diphenylphosphine (4) (scheme II), m.p. 180-183°; ν_{max} 1960(allene) and 1438 cm^{-1} ; ^1H n.m.r.

δ (CDCl_3) 2.90 (2H, d of t, $J_{\text{PCH}} = 8.8$ Hz, $J_{\text{HH}_b} = 2.6$ Hz), 4.80 (2H, m, H_b), 5.36 (1H, m, H_a) and 7.6-7.8 (10H, m, Ph); ^{13}C n.m.r. δ (p.p.m. from TMS; CDCl_3) 23.78 (d, $^{13}\text{CH}_2$, $J_{\text{PC}} = 14.7$ Hz), 70.97 (s, $^{13}\text{CH}_2$), 81.39 (d, $^{13}\text{CH}=\text{C}$, $J_{\text{PCC}} = 10.3$ Hz), 123.9 (m, Ph) and 128.0 (m, Ph); which was converted to the corresponding phosphine oxide, m.p. 208-210°; ν_{max} 1938 (allene) and 1190 cm^{-1} ; m/e 254 (M^+); on treatment with hydrogen peroxide.



Scheme II

The site for phosphide attack is presumably controlled by steric effects (compare reference 2) and this appears to be the first report of a conjugate addition of phosphide anion leading to $\text{S}_{\text{N}}2'$ products. Under certain conditions the reaction of diphenylphosphide with 3-chloropropyne gives products (5) and (6)⁵, which could be explained by similar initial attack on acetylenic carbon. However, the authors have conclusively shown that the reaction involves substitution at saturated carbon followed by base-catalysed prototropic rearrangement. The nature of the products excludes this type of pathway in the reaction of chlorobutadienes with phosphide.



Similar reactions with diphenylarsenide anion gave analogous products, but in low yield. We thank E. I. Du Pont de Nemours and Company for financial support.

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