Phosphorodiamidites as Synthetic Intermediates in the Preparation of Diphenylacetylenes

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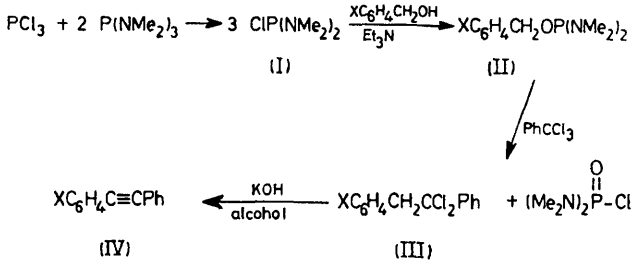
Summary The reaction of benzyl-*NNN'N'*-tetramethylphosphorodiamidite with benzotrichloride provides a convenient synthetic route to diphenylacetylene.

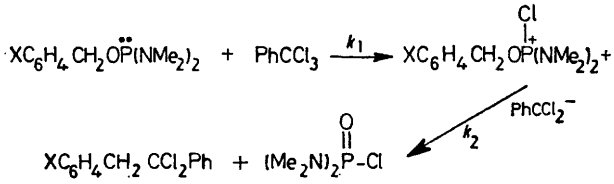
ALTHOUGH diphenylacetylene and its substituted derivatives are well known their syntheses are tedious.[1] We report a convenient route using readily available starting materials which provides diphenylacetylene and its substituted analogues in reasonable yield. The preparation of 1-*p*-methoxyphenyl-2-phenylethyne serves as a typical example (Scheme 1).

PCl_3 (0·082 mol) was added to stirred, ice-chilled hexamethylphosphorous triamide (0·159 mol) under nitrogen. After the addition was complete the ice bath was removed and the mixture was heated at 60 °C for 2 h. The resulting phosphorochloridite[2] (I) was diluted with 60 ml of anhydrous ether, chilled with an ice bath and a solution of *p*-anisyl-alcohol (0·215 mol) and triethylamine (0·236 mol) in 50 ml



SCHEME 1

of anhydrous ether was added dropwise. The mixture was then stirred at room temperature for 8 h, filtered, and evaporated. Benzotrichloride (0·645 mol) was added to the resulting phosphorodiamidite (II), and the mixture was stirred at room temperature for 3 days, producing (III). A solution of KOH (3·2 mol) in ethanol (500 ml) was added and the resulting solution was refluxed overnight, poured into water (1 l), and extracted with ether. The combined ether extracts were dried ($MgSO_4$) and distilled under reduced pressure to remove ethyl benzoate. The residue was chromatographed on silica gel with 3:1 benzene–heptane yielding compound (IV), m.p. 60—61 °C (from MeOH).[3] In other experiments isolation of the phosphorochlorodiamidite (I), the phosphorodiamidite ester (II), and the dichloroethane (III), gave no significant change in the overall yield. A similar preparation using unsubstituted benzyl alcohol gives diphenylacetylene in 62% yield. The dichloroethanes (III; X = Cl) (34% yield) and (III, X = F) (46%) have also been prepared by this method. All compounds gave the expected n.m.r. i.r., and mass spectra. The mechanism postulated for the reaction between phosphorodiamidites and polyhalogenated compounds[4] (Scheme 2) is supported by kinetic data obtained for the reactions of (III, X = H, MeO, Cl and F) with benzotrichloride. Second-order kinetics were observed with rate constants (in benzene at 30·0°) of 0·0594, 0·129, 0·0204, and 0·0391 l mol^{-1} h^{-1} respectively. A Hammett plot of these data yields a ρ value of −2·35 with a correlation coefficient of 0·98. The negative ρ is in accord with the rate-determining nucleophilic attack of the phosphorodiamidite on halogen of the benzotrichloride, followed by a rapid dealkylation of the phosphonium ion (Scheme 2).



Scheme 2

The intermediacy of a polyhalogenated anion is supported by trapping of the trichloromethyl anion as chloroform when (III; X = H) is treated with CCl_4 in the presence of the proton donor methanol. We feel that the convenience of this synthetic scheme compares favourably with those currently available since several substituted benzyl alcohols and benzotrichlorides are commercially available.

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