Nucleophilic Attack by the Diphenylphosphide Ion on Alk-2-ynyl Halides

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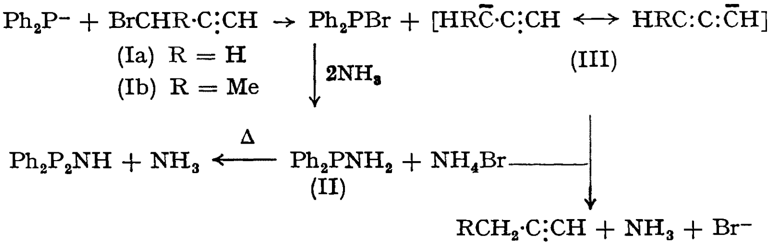
Summary The diphenylphosphide ion in liquid ammonia reacts with alk-2-ynyl halides by nucleophilic attack on bromine in some cases, and in others by nucleophilic attack on carbon.

THE preparation of tertiary phosphines by the reaction of alkali-metal phosphides with alkyl halides is well known.[1] It has been observed, however, that some dialkylphosphides react with 1,2-dihalides giving products arising from the elimination of halogen.[2] We now report examples of nucleophilic attack by the diphenylphosphide ion in liquid ammonia on bromine instead of carbon in monobromo-compounds.



$$\begin{tikzcd}
Ph_2P^- + BrCHR{\cdot}C{\vdots}CH \arrow[r] & Ph_2PBr \arrow[d, "2NH_3"] + [HR\bar{C}{\cdot}C{\vdots}CH \longleftrightarrow HRC{:}C{:}\bar{C}H] \arrow[d] \\
Ph_2P_2NH + NH_3 & Ph_2PNH_2 + NH_4Br \arrow[l, "\Delta"'] \arrow[r] & RCH_2{\cdot}C{\vdots}CH + NH_3 + Br^-
\end{tikzcd}$$

(Ia) R = H

(Ib) R = Me

(II)

(III)

SCHEME

3-Bromoprop-1-yne (Ia) reacts with sodium diphenylphosphide in liquid ammonia to give diphenylphosphinoamine (II) and propyne. No products arising by nucleophilic attack on carbon are found. The amine (II) disproportionates on heating to bis(diphenylphosphino)amine and ammonia.[3] 3-Bromobut-1-yne (Ib) undergoes a similar reaction. We suggest that these reactions proceed by the mechanism shown in the Scheme.

Support for this mechanism is that propyne, from the reaction of the bromide (Ia), is isolated before hydrolysis of the reaction mixture. In addition, the mass spectrum of the crude product from (Ib) showed fragments derived from tetraphenyldiphosphine, which is formed by the competing reaction of sodium diphenylphosphide with diphenylbromophosphine.

Sodium diphenylphosphide reacts with 1-bromobut-2-yne (IV) by nucleophilic attack on carbon to give but-2-ynyldiphenylphosphine (V), (85% yield).

$$\underset{}{Ph_2P^-} + \underset{\text{(IV)}}{BrCH_2{\cdot}C{\vdots}C{\cdot}CH_3} \rightarrow \underset{\text{(V)}}{Ph_2PCH_2{\cdot}C{\vdots}C{\cdot}CH_3} + Br^-$$

The course of these reactions depends on the relative susceptibility of each alkynyl bromide to nucleophilic attack on bromine and on carbon The stability of the carbanion (III)[4] will govern the ease of attack on bromine, and factors affecting S_N2 attack on carbon are well described[5]

Although the bromide (Ia) is known to undergo ready ammonolysis in liquid ammonia,[6] no solvolysis products were found in this study

The corresponding chlorides react with sodium diphenylphosphide in liquid ammonia or tetrahydrofuran by nucleophilic attack on carbon rather than chlorine this further demonstrates the relative susceptibilities of chloro- and bromo-compounds to nucleophilic attack on halogen[7]

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