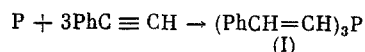


SYNTHESIS OF TRISTYRYLPHOSPHINE FROM RED PHOSPHORUS
AND PHENYLACETYLENE IN A SUPERBASE SYSTEM

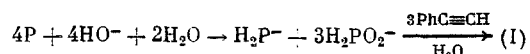
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The reaction of acetylenes with red phosphorus has been carried out for the first time using phenylacetylene. This reaction proceeds upon heating in a superbase medium containing alkali and a polar, aprotic solvent and leads to tristyrylphosphine (I) in 20% yield (the yield was not optimized).



The reaction apparently entails a step involving the formation of deprotonated phosphine species and their nucleophilic addition to the triple bond.



The reaction mechanism, the range of its applicability, and preparative possibilities are under study.

Phosphine (I) was isolated as an oil using preparative thin-layer chromatography on alumina with ether as the eluent. The product purity was 95%. Mass spectrum (m/z): M^+ 340. The PMR signals for the C_6H_5 and $\text{CH}=\text{CH}$ protons in the PMR spectrum taken in CDCl_3 with HMDS as the standard appear at 5.69-7.71 ppm. Found: C, 84.80; H, 6.56; P, 7.69%. Calculated for $\text{C}_{24}\text{H}_{21}\text{P}$: C, 84.70; H, 6.21; P, 9.09%.

Heating phosphine (I) in an air stream gave tristyrylphosphine oxide, mp 248-249°C (from ethanol) [1, 2]. IR spectrum (ν , cm^{-1}): 1220 ($\text{P}=\text{O}$), 1480, 1560, 1600 (Ph , $\text{C}=\text{C}$). Mass spectrum (m/z): M^+ 356. Found: C, 81.67; H, 5.89; P, 8.53%. Calculated for $\text{C}_{24}\text{H}_{21}\text{OP}$: C, 80.88; H, 5.94; P, 8.69%.

The reaction of phosphine (I) with methyl iodide leads to the formation of triphenylphosphonium iodide. PMR spectrum (δ , ppm, J, Hz) in CDCl_3 with HMDS as the internal standard: 7.33-7.13 m ($\text{C}_6\text{H}_5\text{CH}_2$), 6.66 d. d (PCH_2), 1.93 d (CH_3), $J_{\text{H}_A\text{H}_B}$ 13, $J_{\text{H}_A\text{P}}$ 46, $J_{\text{H}_B\text{P}}$ 20.5, $J_{\text{CH}_3\text{P}}$ 12.9. Found: C, 62.23; H, 5.02; I, 25.93; P, 6.36%. Calculated for $\text{C}_{25}\text{H}_{24}\text{IP}$: C, 62.25; H, 5.01; I, 26.32; P, 6.42%.

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