Studies on Ylides: Carbonyl Olefination with Diphenylmethylene-triphenylphosphorane

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Diphenylmethylenetriphenylphosphorane, a stable phosphonium ylide, has been prepared and reacted with a range of substituted aromatic aldehyde to afford 1,1,2-triaryl-substituted ethylenes in fair to good yields. The structure of the products are based on IR and NMR spectral evidence.

Although the stability and reactivity of diphenylmethylenetriphenylphosphorane (1) has long been of interest, however, the reactivity of ylide (1) towards normal carbonyl compounds, has been relatively little explored until recently.

Earlier in 1919 Staudinger and Meyer showed that the reaction of ylide (1) with phenylisocyanate gave N-phenyldiphenylketeneimine, but this discovery did not lead to the discovery of a new synthesis of olefins. Similarly it has been found that the reaction of ylide (1) with diphenyl ketene occurs only under forcing conditions. Recently Brososvki et al. investigated the reaction of 1 with nitrosobenzene to afford desired Wittig reaction products.

With a view to examine the reactivity and synthetic potentialities of 1 in carbonyl olefination, following our previous researches on the reactions of ylides, we have developed the reaction conditions under which 1 reacted with a ranged aromatic aldehydes in a facile manner to afford 1,1,2-triaryl substituted ethylenes.

Results and Discussion

Quaternization of triphenylphosphine with diphenylmethyl bromide in benzene at a reflux temperature gave diphenylmethyltriphenylphosphonium bromide (2) in fair yield. Treatment of 2 with a suspension of sodium ethoxide in ether effected the proton abstraction affording red crystalline solid of 1. 1 was isolated at room temperature in pure form, however, on exposure to room temperature, turns to a dark-green coloured solid. Hence all the reactions were carried out in benzene solution under an atmosphere of dry nitrogen. A convenient procedure for the reaction of 1 with aromatic aldehydes consists of adding a etherial suspension of sodium ethoxide to a etherial solution of 2 to afford 1 as red solid. As the substituted aromatic aldehyde was added in benzene solution, precipitate of triphenylphosphine oxide was formed. The 1,1,2-triaryl-substituted ethylenes (3a-j) were isolated by chromatographic separation of the filtrate through neutral alumina (Scheme 1).

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Scheme 1.

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\begin{align*}
\text{Ph}_3\text{P} - \text{CH}_9 \quad \text{Ph}_3\text{P} - \text{C}^\circ \quad \text{Ph}_3\text{P} - \text{C}^\circ \\
\text{Br} \quad \text{C}_9\text{H}_5 \quad \text{NaOEt} \quad \text{C}_9\text{H}_5 \\
\text{ether} \quad \text{ether} \quad \text{ether} \\
\text{1} \quad \text{1} \quad \text{1} \\
\text{ArCHO} \quad \text{ArCHO} \quad \text{ArCHO} \\
3a-\text{j} \quad 3a-\text{j} \quad 3a-\text{j} \\
\text{ArCH} = \text{C} \quad \text{ArCH} = \text{C} \quad \text{ArCH} = \text{C} \\
\text{Ar} = \text{C}_9\text{H}_5, \quad \text{Ar} = \text{C}_9\text{H}_5, \quad \text{Ar} = \text{C}_9\text{H}_5, \\
\text{Ar} = 2-\text{OCH}_3\text{C}_6\text{H}_4, \quad \text{Ar} = 2-\text{OCH}_3\text{C}_6\text{H}_4, \quad \text{Ar} = 2-\text{OCH}_3\text{C}_6\text{H}_4, \\
\text{Ar} = 4-\text{CH}_3\text{C}_6\text{H}_4, \quad \text{Ar} = 4-\text{CH}_3\text{C}_6\text{H}_4, \quad \text{Ar} = 4-\text{CH}_3\text{C}_6\text{H}_4, \\
\text{Ar} = 2,4-(\text{Cl})_2\text{C}_6\text{H}_3, \quad \text{Ar} = 2,4-(\text{Cl})_2\text{C}_6\text{H}_3, \quad \text{Ar} = 2,4-(\text{Cl})_2\text{C}_6\text{H}_3, \\
\text{Ar} = 2-\text{OH}-1\text{-naphthyl.} \quad \text{Ar} = 2-\text{OH}-1\text{-naphthyl.} \quad \text{Ar} = 2-\text{OH}-1\text{-naphthyl.}
\end{align*}
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All the 1,1,2-triaryl-substituted ethylenes (3a–j) synthesized by the above procedure are listed in Table I. The versatile applicability of 1 in carbonyl olefination is obvious from the inspection of Table I. Best results are obtained when electron-withdrawing substituents are attached at carbonyl function. The ethylenes (3a–j) gave satisfactory elemental analysis. Structures of the products are based on IR and NMR spectroscopy.

The IR spectra (KBr) of 3a–j, along with the other absorption bands, showed characteristic absorption bands at 1610 cm⁻¹ (ν C=O) and at 3050 cm⁻¹. The NMR spectra (CDCl₃) in general, exhibited a complex pattern of absorption of olefinic and aromatic protons in between δ 6.80–8.33.

**Experimental**

Melting points were determined on a Gallenkamp apparatus and are uncorrected. IR spectra (KBr) were recorded on a Perkin-Elmer infracord instrument. NMR spectra (CDCl₃) were run on a Varian A-60 spectrometer using TMS as an internal standard and are reported in δ (ppm) values. All the products were separated and purified by column chromatography using alumina. Unless otherwise stated all the reactions were carried out under dry nitrogen.

**Preparation of diphenylmethyltriphenylphosphonium bromide (2)**

A solution of 12.35 g (0.05 mole) of diphenylmethyl bromide and 13.10 g (0.05 mole) of triphenylphosphine in 100 ml of benzene was heated under reflux on a water bath for 1 h. The resulting solid was separated by filtration and recrystallized from chloroform-ethylacetate (1:4) to give white microcrystals of 2, m.p. 227–228 °C (dec.)(Lit. 7 230 °C (dec.).) yield 17.53 g (70%). (C₃₁H₂₆PBr). Found C 73.05 H 5.09, Caled. C 73.08 H 5.10.

**Preparation of diphenylmethylenetriphenylphosphorane (1)**

A suspension of dry sodium ethoxide (prepared from 0.15 g of sodium and 10 ml of ethanol) in 20 ml of ether was added to a solution of 5.09 g (0.01 mole) of 2 in 80 ml of ether. The reaction mixture was stirred at room temperature under nitrogen for 3 h. Resulting red coloured solution was concentrated under reduced pressure and cooled in an ice-salt freezing mixture to afford red needles 2.5 g (60%) of 1. It was further purified by recrystallization from benzene-hexane mixture (1:4) to give red crystals. m.p. 170–172 °C (Lit. 7 172 °C).
Reaction of ylide (1) with aromatic aldehydes (general procedure) (Table I)

In all the reactions freshly prepared ylide was used. To a stirred solution of 4.28 g (0.01 mole) of 1 in 80 ml of benzene, was added under nitrogen 0.01 mole of aromatic aldehyde. The mixture was heated under reflux for 5 h and was allowed to stand overnight at room temperature. The residue containing triphenylphosphine oxide was filtered off and the filtrate was concentrated on a steam bath under reduced pressure. The resulting product was chromatographed to afford corresponding 1,1,2-triaryl-substituted ethylene (3a–j), which was further purified by crystallization from appropriate solvent.

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