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THE STEREOSPECIFIC ADDITION OF ORGANOPHOSPHIDES TO TERMINAL ALKYNES

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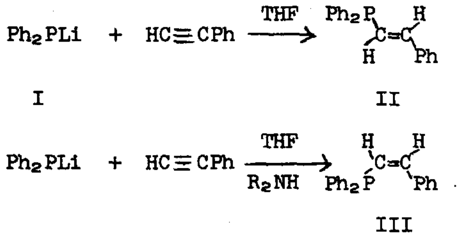
We wish to report that phenylacetylene adds lithium diphenylphosphide (I) in tetrahydrofuran (THF) to give mostly trans-β-styryldiphenylphosphine (II) (b.p. 198-200° at 1.6 mm), as shown by vapor phase chromatography at 210° employing a 4' 3% SE-30 column, while cis-β-styryldiphenylphosphine (III) (m.p. 90-92°) is isolated in 70% yield when a primary or secondary amine (e.g. butylamine or diethylamine) is added to the reaction mixture (Eq. 1).



Equation 1.

Anal. Calcd. for $C_{20}H_{17}P$: C, 83.33; H, 5.90; P, 10.76. Found: C, 83.52; H, 6.08; P, 10.64.

Tertiary amines show no effect. The reaction is not due to addition of diphenylphosphine (IV) formed from a proton exchange between the alkyne and I (Eq. 2).

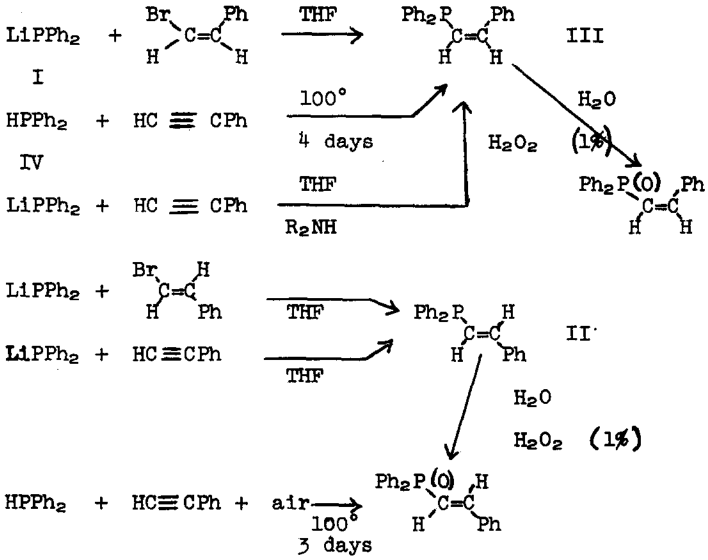
$$\underset{\mathrm{I}}{Ph_2PLi} + HC\equiv CPh \overset{THF}{\rightleftharpoons} \underset{\mathrm{IV}}{Ph_2PH} + LiC\equiv CPh$$

Equation 2.

This is true because IV does not react with phenylacetylene after many hours of being subjected to these conditions. Although Hoffmann[2] has reported the addition of IV to phenylacetylene after seven days at 100°, in the absence or air, to give a β-styryldiphenylphosphine (m.p. 89-90°), and after three days in the presence of air to give a β-styryldiphenylphosphine oxide (m.p. 165-67°), nothing was said of the stereochemistry of these compounds. Comparison of the melting point of this oxide with those of the now known cis- and trans-β-styryldiphenylphosphine oxides[3,4] shows that the trans-isomer was isolated.

Comparison of the melting point of the phosphine isolated by Hoffmann with that of the phosphines isolated by us from the reactions of cis-β-bromostyrene or phenylacetylene (in the presence of amine) with I shows all to be identical. Repetition of the reaction of IV with phenylacetylene at 100° for four days in this laboratory also led to the same material. Mild oxidation of this phosphine (III) with dilute aqueous peroxide led to the known cis-β-styryldiphenylphosphine oxide.[4] Isomer II was also prepared from trans-β-bromostyrene and I. Unlike

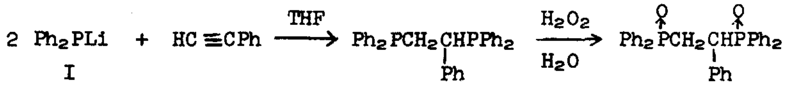
III it was found to be an air sensitive liquid giving rise to trans-β-styryldiphenylphosphine oxide. This is summarized in Equation 3.



Equation 3.

Proton magnetic resonance spectra taken of III in deuteriochloroform solution at 60 Mc shows a single phenyl proton complex at $\tau = 2.7$ and a quartet centered at $\tau = 3.58$ due to a vinyl proton ($J = 12.8$ and 2.2). Decoupling work is being done to establish the origin of these couplings, but it would appear that III has an abnormally low J_{PH} (gem) (2.2 cps). The signal for the other vinyl proton signal is hidden under the phenyl complex. The relative area ratio for the phenyl complex to the vinyl proton signal is 16:1. Spectra of II taken in $DCCl_3$ show a single phenyl complex centered at $\tau = 2.75$ which partially overlaps a doublet at $\tau = 3.0$ ($J = 11$ cps). No area ratio is obtainable.

When two moles of I are allowed to react with phenyl acetylene in THF over a period of hours, phenylethylenebis(diphenylphosphine) is isolated as the dioxide (V) in 15-20%[4] (Eq. 4).

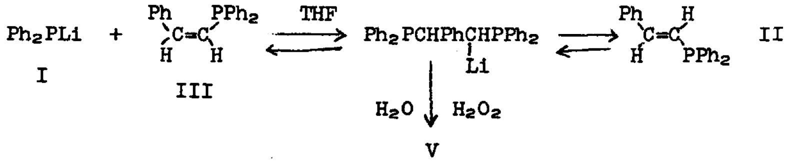


$$\underset{\mathrm{I}}{2\ \mathrm{Ph_2PLi}} + \mathrm{HC{\equiv}CPh} \xrightarrow{\mathrm{THF}} \mathrm{Ph_2PCH_2}\underset{\mathrm{Ph}}{\mathrm{C}}\mathrm{HPPh_2} \xrightarrow[\mathrm{H_2O}]{\mathrm{H_2O_2}} \mathrm{Ph_2}\overset{\mathrm{O}}{\mathrm{P}}\mathrm{CH_2}\underset{\mathrm{Ph}}{\mathrm{C}}\mathrm{H}\overset{\mathrm{O}}{\mathrm{P}}\mathrm{Ph_2}$$

V

Equation 4.

Most of the remainder is the trans isomer II. The reversible addition of I to initially produced III may account for the formation of V, as well as isomerization to II (Eq. 5).



Equation 5.

Reaction of III with I in THF does result in isomerization to II, as well as addition to give V in 15-20% yield, after a period of several hours.

Whereas IV does not add to octyne-1 after 4 days at 100°, I does react with octyne-1 in THF to give only one product (VPC) whose proton NMR spectrum indicates it to be a 1-octenyldiphenylphosphine (VI)(b.p. 190-193° at 1.25 mm)(Eq. 6).

$$\underset{\mathrm{I}}{\mathrm{Ph_2PLi}} + \mathrm{HC{\equiv}C(CH_2)_5CH_3} \xrightarrow{\mathrm{THF}} \underset{\mathrm{VI}}{\mathrm{Ph_2PCH{=}CH(CH_2)_5CH_3}}$$

Equation 6.

The proton NMR spectrum shows a complex centered at τ 2.8 assigned to the phenyl protons, a complex from τ 3.5 to τ 4.5 assigned to the vinyl protons, and three complexes for the methylene and methyl protons which overlap and are centered at τ 7.9, τ 8.7, and τ 9.15. Relative areas are 10:2:13, respectively.

Bubbling acetylene into a THF solution of I leads to ethylenebis(diphenylphosphine)(VII)(Eq. 7).

$$\underset{\text{I}}{2\ \mathrm{Ph_2PLi}} + \mathrm{HC{\equiv}CH} \xrightarrow{\text{THF}} \underset{\text{VII}}{(\mathrm{Ph_2PCH_2})_2}$$

Equation 7.

Complex formation between the amine and I or an organolithium compound formed after addition probably causes the change in stereochemistry of the resulting vinylphosphine. Polymerization of olefins by organolithiums is known to show marked changes in stereospecificity when bases are added.[5]

The ineffectivness of amine addition in the cases of octyne-1 and acetylene suggests a different mechanism from that in operation when an electron sink such as a phenyl group is present on the alkyne.

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