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REACTION OF DIPHENYLACETYLENE WITH ORGANOPHOSPHIDES. A STEREOSPECIFIC SYNTHESIS OF VINYL PHOSPHINES.

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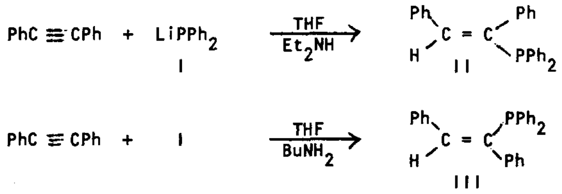
Lithium diphenyl phosphide(I) (prepared from the alkali metal and diphenylphosphinouschloride in tetrahydrofuran) has been found to react with diphenylacetylene to give high yields of stereochemically pure vinyl phosphines in the presence of a primary or secondary amine. The stereochemistry of the phosphine produced depends solely upon the amine used and is reversed upon going from a primary to a secondary amine.

Diphenylacetylene reacts very exothermically with I in the presence of a tertiary amine or in the absence of amines to produce a highly colored solution which leads to intractable syrups. There is no observable stoichiometry for this reaction. Anionic and/or radical polymerization seems to occur. Addition of a secondary amine (e.g. diethylamine or N-methylaniline) to either reagent prior to reaction leads to isolation of cis-1,2-diphenylvinyldiphenylphosphine(II), m.p. 114-115 (hexane) in 90% yield. Anal. Calcd. for $C_{26}H_{21}P$: C, 85.69; H, 5.80; P, 8.53. Found: C, 85.38; H, 5.82; P, 8.80. This reaction is only very slightly exothermic and shows a slow dissipation of the red color of I to a brown. (Eq. 1.)



Equation 1.

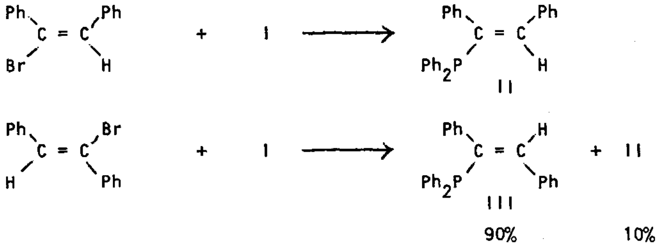
A similar reaction occurs when a primary amine (e.g. butylamine) is added to either reactant, but the product obtained in 80% yield is the isomeric *trans*-1,2-diphenylvinyldiphenylphosphine(III), m.p. 120-121 (MeOH). (Eq. 1.) Anal. Calcd.: same as for II. Found: C, 86.02; H, 5.59. This isomer is unstable to ethanol recrystallization and results in isolation of II when attempted.

The stereochemical purity of these reactions was verified by vapor-phase chromatography on a 3% SE 30 column at 210°. The reaction mixture with a secondary amine gave only II and the one with a primary amine gave only III. These conditions do not isomerize II or III.

Treatment of II and III in acetone with 3% hydrogen peroxide gave *cis*-1,2-diphenylvinyldiphenylphosphine oxide (IIa), m.p. 153-154 (MeOH), and *trans*-1,2-diphenylvinyldiphenylphosphine oxide (IIIa), m.p. 224-225, respectively. Anal. Calcd. for $C_{26}H_{21}PO$: C, 82.09; H, 5.56. Found; for IIa, C, 81.49; H, 5.48, and for IIIa, C, 82.51; H, 5.68.

Stereochemical assignments are made on the basis of independent preparation and nmr data. The reaction of I with vinyl halides has been shown to proceed stereospecifically with retention of configuration.[2]

Cis- and *trans*-α-bromostilbenes[3,4] were prepared and reacted with I. *Cis*-α-bromostilbene gave only II as shown by VPC analysis. *Trans*-α-bromostilbene gave both II and III in a ratio of 1:9. The production of this small amount of II might occur from loss of HBr from the *trans*-α-bromostilbene followed by addition of I to the diphenylacetylene thus produced. (Eq. 2.)



Equation 2.

Proton nmr spectra of II in deuteriochloroform solution at 60 Mc show a complex signal centered at $\tau = 2.65$ and a sharp peak at $\tau = 3.06$ assigned to the phenyl protons, and a doublet centered at $\tau = 3.45$ ($J = 10$ cps) assigned to the vinyl proton. Relative areas are 15:5:1, respectively, showing that the signal from one of the two phenyls on the vinyl group is hidden under the proton signal from the phenyls on the phosphorus. Comparison of this spectrum with those of *cis*- and *trans*-β-styryldiphenylphosphines (isolated from the reaction of I with *cis*- and *trans*-β-bromostyrene, respectively)[2,5,6] indicate the β-phenyl to be hidden since both of these compounds show only one phenyl proton complex.

Anderson, Freeman and Reilly[7] have shown $J_{PH(cis)} = 13.6$ cps and $J_{PH(trans)} = 30.2$ cps, for trivinylphosphine. The coupling constant of 10 cps found in II indicates that the vinyl hydrogen is <u>cis</u> to the phosphorus.

Proton nmr spectra of III show only a phenyl complex centered at $\tau = 2.7$ and a sharp peak at $\tau = 3.05$. The relative ratio is 16:5, indicating that the vinyl proton signal is hidden under the signal from the β-phenyl and the two phenyls on the phosphorus.

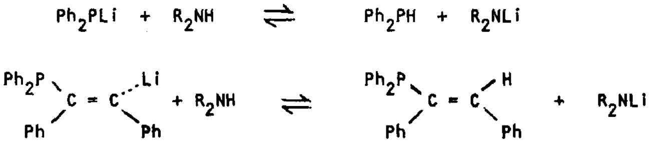
Either oxide (IIa or IIIa) may be isomerized to a mixture of IIa and IIIa by PCl_3. Treatment of II or III with HBr in glacial acetic acid[8] results in auto-oxidation reduction to yield 1,2-diphenylethyldiphenylphosphine oxide.[9] (Eq. 3.)

$$Ph_2PCPh = CHPh \xrightarrow[HOAc]{HBr} x \xrightarrow{H_2O} Ph_2\overset{(O)}{P}CHPhCH_2Ph$$

Equation 3.

Diphenylphosphine will not react with diphenylacetylene under these reaction conditions, but it will react in a sealed tube at 100° for four days to yield only III as shown by VPC analysis of the reaction mixture.

Addition of an amine to I causes no visible reaction and good yields of diphenylphosphinic acid (after treatment with 3% aqueous hydrogen peroxide) or benzyldiphenylphosphine oxide (after reaction with benzyl chloride followed by peroxide) may be obtained. Any acid-base equilibrium which might be set up between the amine and I would be expected to favor the phosphide over the amide since the latter is the stronger base. The reaction of the vinyl carbanion which may be formed upon addition of I to the triple bond, with the amine may be important since there is little deuterion incorporation (as shown by nmr) if the reaction is quenched after 10 minutes with D_2O, nor is there any ethylation by ethylbromide if it is added after I has completed reacting, even though as exothermic reaction results. (Eq. 4.)



Equation 4.

Since the reaction of sodium diphenylphosphide (prepared the same as I using sodium metal) with diphenylacetylene is unchanged whether a primary or secondary amine is used and yields only III, it is possible that the roll of the amine is to complex the lithium ion of I and make it more ionic and thus more like the sodium reagent. It would seem that I, in a more covalent state, adds to π systems in a cis manner and in a more ionic state in a trans fashion. Further investigation of the addition of I to π systems is in progress.

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