

LITHIUM CLEAVAGE OF UNSATURATED VICINAL DI-*tert*-PHOSPHINES

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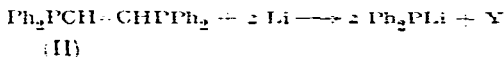
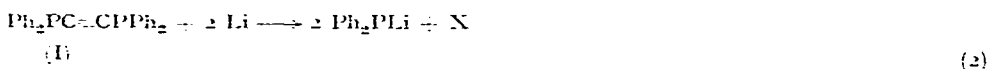
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The cleavage of tertiary phosphines by alkali metals to give metallo-organophosphides and organometallics is well known<sup>1,2,3</sup>. Issleib<sup>1</sup> has suggested that the reaction of alkali metals with tertiary phosphines, containing at least one aromatic group bonded to phosphorus, proceeds by the initial formation of a dimetallophosphorane  $R_3PM_2$  which dissociates to the alkali metal organophosphide,  $MPR_2$ , and the organometallic,  $RM$ . The claim was made<sup>1</sup> that the dissociation of the dimetallo adduct takes place stepwise as indicated by electron resonance studies of the paramagnetic intermediate  $(PhC_6H_4)_3PM$  obtained from the stable diadduct of tris(biphenyl-1)phosphine  $(PhC_6H_4)_3PM_2$ . Issleib has concluded that when mixed tertiary phosphines are used, cleavage occurs at that carbon-to-phosphorus bond which leads to the ejection of the most "electronegative" group and an organophosphide containing at least one aromatic group<sup>1</sup>. In compounds where the two effects would lead to different products, the product obtained is that in which the organophosphide contains at least one aromatic group (eqn. 1).

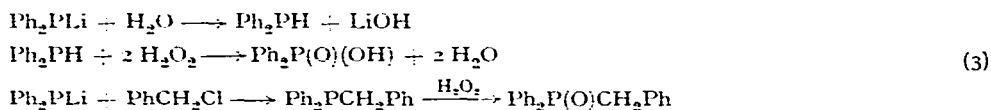


Alkali metal cleavage of mixed tertiary aryl phosphines containing vinyl or ethynyl groups bonded to phosphorus have not been studied.

We have found that lithium in tetrahydrofuran causes cleavage of the phosphorus-to-olefin carbon bond, rather than the phenyl-to-phosphorus bond, in ethynyl-enebis(diphenylphosphine), (I), and *cis*- or *trans*-1,2-vinylenebis(diphenylphosphine), (II) (eqn. 2).

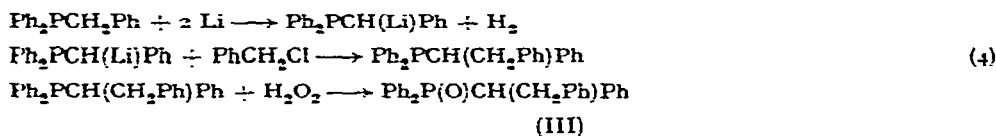


Support for this formulation comes from the fact that treatment of the red reaction solution with dilute aqueous peroxide or benzyl chloride leads to diphenylphosphinic acid and benzyldiphenylphosphine (isolated as the oxide), respectively, in good yields (eqn. 3).

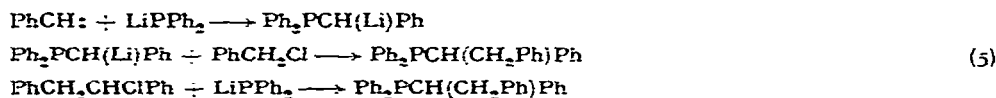


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When a large excess of lithium metal is used, (1,2-diphenylethyl)diphenylphosphine oxide (III) is also isolated<sup>4</sup>. This material may result from the reaction of benzyldiphenylphosphine and lithium to give rise to ( $\alpha$ -lithiobenzyl)diphenylphosphine which is then benzylated by benzyl chloride (eqn. 4)<sup>4</sup>.

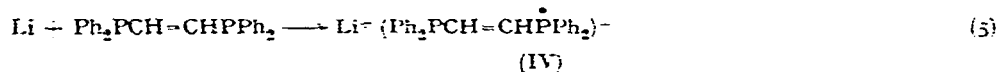


Reaction of the benzyl chloride with lithium might conceivably lead to benzylmethylene or  $\alpha$ -chlorobibenzyl which would then react with lithium diphenylphosphide to produce the product (eqn. 5).

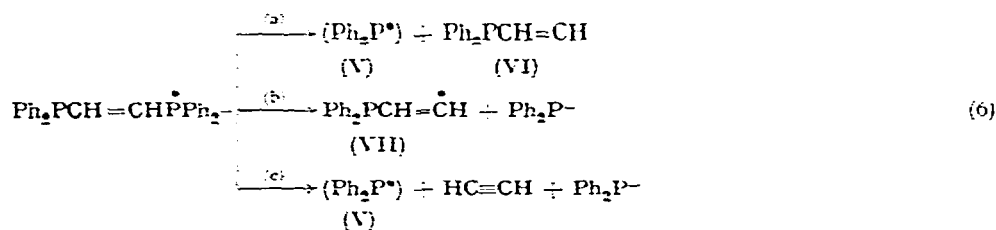


Exact formulations for the nature of X and Y (eqn. 1) are not yet possible. Production of black solid, believed to be carbon, was noted in the cleavage of the ethynylenebis compound (I). There was no indication of the production of hydrocarbons when the reaction solution of (I) and lithium was treated with benzyl chloride. No hydrocarbon was isolated from similar treatment of (II).

Assuming initial donation of an electron from the lithium metal to (II) and choosing to depict the odd electron as being located at a phosphorus atom (independent of the mode and location of initial donation), radical anion (IV) would be formed (eqn. 5).



Bonding of the lithium metal with (IV) may be covalent at either phosphorus or carbon or ionic, as depicted in eqn. (5) for focus of attention on (IV). Decomposition of (IV) to produce the products obtained could occur by a variety of paths (eqn. 6).



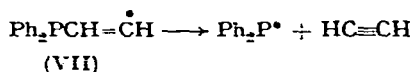
Reduction of the phosphorus radical (V) by lithium to produce lithium diphenylphosphide is expected (eqn. 7).



Coupling of these radicals to tetraphenylbiphosphine would still lead to lithium diphenylphosphide in the presence of lithium (eqn. 8)<sup>1</sup>.

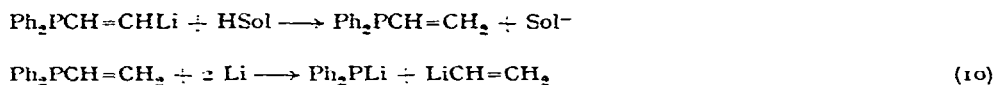


Intermediates (VI) and (VII) might be expected to undergo  $\beta$ -elimination of diphenylphosphide ion and diphenylphosphorus radical (V), respectively, in boiling tetrahydrofuran (eqn. 9).

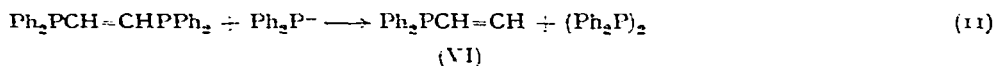


In view of the stability of the lithium salt of ethynyl-dibutylphosphine in liquid ammonia<sup>5</sup> and of ethynyl-diphenylphosphine in boiling alcoholic potassium hydroxide or fused alkali,  $\beta$ -decomposition of (VI) seems unlikely<sup>5,6</sup>.

Protonation of (VI) by the solvent, followed by further cleavage of the vinyl-diphenylphosphine thus produced would also lead to lithium diphenylphosphide (eqn. 10).

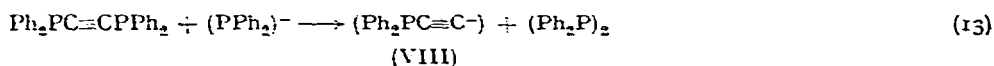
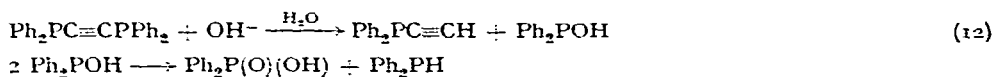


After initiation of the reaction, the lithium diphenylphosphide produced might then attack the diphosphine at the phosphorus atom, causing ejection of (VI) and production of tetraphenylbiphosphine (eqn. 11).



Reaction of excess lithium diphenylphosphide produced from chlorodiphenylphosphine, with (II) in boiling tetrahydrofuran for two hours led to the complete recovery of the diphosphine, showing that cleavage of the vinyl-to-phosphorus bond by nucleophilic attack on the phosphorus by diphenylphosphide does not occur.

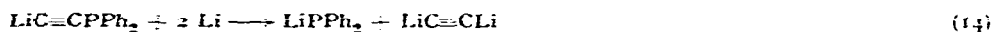
Hartmann's report<sup>6</sup> that boiling alcoholic alkali or fused alkali cleaves ethynyl-enebis(diphenylphosphine) to ethynyl-diphenylphosphine and diphenylphosphinous acid (eqn. 12) indicates that, unlike vinyl-enebis(diphenylphosphine), the acetylenic compound would be expected to be susceptible to attack by any diphenylphosphide initially produced (eqn. 13).



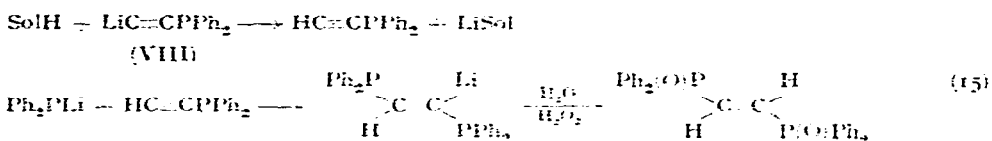
Reaction of (I) with excess lithium diphenylphosphide (produced from chlorodiphenylphosphine) in boiling tetrahydrofuran led to the isolation of diphenylphosphinic acid in excess of that expected from the chlorodiphenylphosphine used, in an amount equivalent to 31% of the total phosphorus, or 62% of one of the phosphorus atoms in the ethynylenebis(diphenylphosphine). Aside from diphenylphos-

phinic acid and a small amount of *trans*-vinylenebis(diphenylphosphine) dioxide (12%), only benzene-soluble material was obtained. Ethynylenebis(diphenylphosphine) dioxide is produced from (I) under the conditions used in the work up of this experiment. Thin-layer chromatography showed that no ethynylenebis(diphenylphosphine) dioxide was present in the benzene soluble fraction and that this fraction consisted of three major and one minor components. It can be concluded that (I) did not survive treatment with lithium diphenylphosphide.

One possible explanation for these results is indicated in eqn. (13). The cleavage products would then arise from the reaction of lithium metal with (VIII) (eqn. 14).



Solvent protonation of a small amount of (VIII) would lead to ethynyldiphenylphosphine which would be expected to add lithium diphenylphosphide, giving rise to *trans*-vinylenebis(diphenylphosphine) dioxide (eqn. 15).



## EXPERIMENTAL

### Lithium cleavage of 1,2-ethynylenebis(diphenylphosphine)<sup>6</sup>

(a). *Followed by treatment with water.* 1,2-Ethynylenebis(diphenylphosphine) (0.5 g, 0.0027 mole) and 0.3 g lithium (0.0428 g-atom) were refluxed for 2 h in 25 ml tetrahydrofuran (CaH<sub>2</sub>-dried) under a nitrogen atmosphere with no apparent reaction. Addition of a catalytic amount of sodium gave similar results. Further addition of freshly cut lithium (0.15 g, 0.0214 g-atom) produced a dark red solution. The excess lithium was filtered off after two additional hours of refluxing, and the solution added to 50 ml hydrogen peroxide (3%) and 50 ml water. After 12 h the clear basic solution was acidified with enough 6 N hydrochloric acid to produce cloudiness. The solid thus precipitated was diphenylphosphinic acid (0.48 g, 87% yield) as shown by mixture melting point, and infra-red spectrum comparison with authentic material.

(b). *Followed by treatment with benzyl chloride.* When the above reaction solution was decolorized by addition of benzyl chloride, diphenylphosphinic acid (21%) and benzyldiphenylphosphine oxide (76%) were isolated, as shown by mixture melting point and infra-red and proton magnetic resonance spectrum comparison with authentic material.

### Lithium cleavage of vinylenebis(diphenylphosphines)<sup>7</sup>

(a). *Followed by treatment with water.* To a suspension of 9.2 g (0.0231 mole) of *trans*-vinylenebis(diphenylphosphine) in 200 ml of dry tetrahydrofuran was added, under nitrogen, 1.2 g (0.18 g-atom) of lithium metal. The colorless mixture was heated to reflux for 30 min and no change noted other than the coating of the lithium metal. Addition of another 1.2 g of lithium and refluxing gave no change after 30 min. Addition of a small amount of sodium caused the production of a yellow color after 10 min of refluxing. After adding 50 ml of dry benzene and 0.5 g of lithium and further

heating to reflux, a deep red color was produced. The mixture was refluxed for 2 h and cooled to room temperature, the excess lithium was removed by filtration and most of the tetrahydrofuran distilled off at atmospheric pressure under nitrogen. To the remaining red syrup was added 50 ml of water and 100 ml of 3% aqueous hydrogen peroxide. The resulting clear, aqueous solution was basic to litmus and, upon acidification with dilute HCl, yielded a heavy white precipitate. Filtration and recrystallization from 95% ethanol afforded 7.7 g (76%) of diphenylphosphinic acid, m.p. 175–80°, characterized by infra-red comparison. The same procedure was employed with *cis*-1,2-vinylenebis(diphenylphosphine) omitting the benzene since the *cis* isomer is more soluble in tetrahydrofuran, and diphenylphosphinic acid was obtained in 74% yield.

(b). *Followed by treatment with benzyl chloride.* Approximately 0.1 mole of *trans*-vinylenebis(diphenylphosphine) was made from lithium diphenylphosphide (obtained from 52.4 g or 0.2 mole of triphenylphosphine) and 10 g (0.1 mole) of *trans*-dichloroethene in tetrahydrofuran. To this reaction solution was added 3.6 g (0.8 g-atom) of lithium metal and a small piece of sodium metal. The reaction mixture was refluxed for 1.5 h. The usual deep red color was produced early in the reflux period and a gas was evolved.

A solution of 25.2 g (0.2 mole) of benzyl chloride in 20 ml tetrahydrofuran was added dropwise. Although the addition was highly exothermic, the red color was not discharged. An equal amount of benzyl chloride was added dropwise and only after about 40% of this was added was the color essentially discharged. Addition of the reaction mass to 3% hydrogen peroxide, evaporation of volatile materials and filtration led to isolation of 30 g of a solid, m.p. 185–90°. Gas-chromatographic analysis indicated that the composition of this material was about 60% benzyldiphenylphosphine oxide and 40% (1,2-diphenylethyl)diphenylphosphine oxide. This represents a yield of 20.5% benzyldiphenylphosphine oxide and 23.6% (1,2-diphenylethyl)diphenylphosphine oxide, assuming all of the sample went through the column.

#### *Reaction of lithium diphenylphosphide with vinylenebis(diphenylphosphine)*

A 5.5% portion of a solution of lithium diphenylphosphide in tetrahydrofuran, representing 0.0055 mole of the total made from 22.0 g (0.1 mole) of chlorodiphenylphosphine and excess lithium metal, was refluxed with 2.0 g ( $5.05 \times 10^{-3}$  mole) of a mixture of *cis*- and *trans*-vinylenebis(diphenylphosphine) under nitrogen for 2 h. The red color was never discharged. After cooling to room temperature, the reaction mixture was added to a dilute aqueous peroxide solution and the tetrahydrofuran evaporated. Filtration of the solid thus produced led to the isolation of 2.1 g ( $4.9 \times 10^{-3}$  mole) of solid identified as a mixture of *cis*- and *trans*-vinylenebis(diphenylphosphine) dioxide by infra-red spectra and melting point comparison with authentic material. This represents a 97% recovery of starting diphosphines. Acidification of the basic aqueous filtrate led to the isolation of 0.7 g ( $3.2 \times 10^{-3}$  mole) or about 60% of the maximum theoretical yield of diphenylphosphinic acid obtainable from the amount of lithium diphenylphosphide used if 100% conversion of chlorodiphenylphosphine to lithium diphenylphosphide is assumed.

#### *Reaction of lithium diphenylphosphide with ethynylenebis(diphenylphosphine)*

An 8-ml portion of a tetrahydrofuran solution containing  $6.4 \times 10^{-3}$  mole of

lithium diphenylphosphide (prepared from chlorodiphenylphosphine and lithium metal) was added to 20 ml of tetrahydrofuran containing 1.5 g ( $3.8 \times 10^{-3}$  mole) of ethynylenebis(diphenylphosphine) and the solution refluxed for 2 h. No decolorization had occurred. Cooling to room temperature, addition of 5 ml of 3% hydrogen peroxide, addition of enough water to bring the total volume to 100 ml and evaporation of the tetrahydrofuran led to the separation of an oil. The oil was extracted with chloroform.

Acidification of the basic aqueous layer gave 1.9 g ( $8.72 \times 10^{-3}$  mole) of diphenylphosphonic acid or  $2.32 \times 10^{-3}$  mole more acid than the maximum obtainable from the lithium diphenylphosphide used. This represents about 31% of the total phosphorus or 62% of one of the phosphorus atoms in the starting diphosphine.

Evaporation of the chloroform solution gave an oil which upon treatment with benzene precipitated 0.2 g ( $4.66 \times 10^{-4}$  mole, 12%) of *trans*-vinylenebis(diphenylphosphine) dioxide identified by melting point, infra-red spectrum and proton nuclear magnetic spectrum.

The benzene-soluble portion left a syrup upon evaporation. The infra-red spectrum of a chloroform solution of this material showed it to contain tertiary phenylphosphine oxides. Thin-layer chromatography employing chloroform as the eluent, showed this fraction to consist of three major and one minor components, none of which displayed the same  $R_F$  as authentic ethynylenebis(diphenylphosphine) dioxide.

#### ACKNOWLEDGEMENTS

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#### SUMMARY

Lithium metal in tetrahydrofuran has been found to react with ethynylenebis(diphenylphosphine) and *cis*- or *trans*-1,2-vinylenebis(diphenylphosphine) to produce lithium diphenylphosphide in high yield. Possible mechanistic paths are discussed. In this connection the reactions of the vinylenebis- and ethynylenebis(diphenylphosphines) with lithium diphenylphosphide have been examined and the results are discussed.

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