49. (2,2-DIMETHYLPROPYLIDYNE)PHOSPHINE

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(2,2-Dimethylpropylidyne)phosphine is the first compound with a phosphorus–carbon triple bond stable at room temperature.[1] Since the electronegativities of phosphorus (2.2) and carbon (2.5) differ substantially from the value of nitrogen (3.0), the compound is more likely to react as the analog of an alkine than of a nitrile. Thus far, the reactivity of the phosphine

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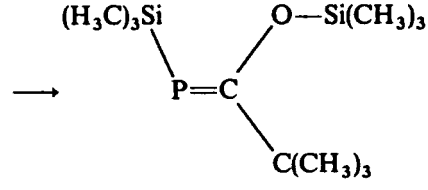
towards transition metal complexes with the metals in low oxidation states[2] and towards organic 1,3-dipolar[3] or Diels–Alder reagents,[3,4] has been studied. With halides of main group and subgroup elements[5] numerous insertion reactions have been observed; from the addition of lithium bis(trimethylsilyl)phosphide·2tetrahydrofuran (THF) in 1,2-dimethoxethane (DME), lithium 3,5-di-*tert*-butyl-1,2,4-triphospholid·3DME can be obtained.[5,6]

A. [2,2-DIMETHYL-1-(TRIMETHYLSILOXY)PROPYLIDENE]-(TRIMETHYLSILYL)PHOSPHINE[7,*]

$$[(H_3C)_3Si]_3P \xrightarrow[-(H_3C)_3SiCl]{+(H_3C)_3CCOCl} [(H_3C)_3Si]_2PCOC(CH_3)_3$$



■ **Caution.** *[2,2-Dimethyl-1-(trimethylsiloxy)propylidene](trimethylsilyl)phosphine, a malodorous liquid, is extremely sensitive to moisture and ignites in air. Therefore, all procedures must be carried out under an atmosphere of dry argon in a well-ventilated fume hood.*

Procedure

In a 500-mL round-bottomed flask connected to the argon–vacuum supply *via* a side arm with a stopcock, 50.0 g (0.20 mol) of tris (trimethylsilyl)phosphine (see Section 48) is dissolved in 200 mL of $LiAlH_4$-dried pentane. At room temperature, 26.5 g (0.22 mol; 10% excess) of 2,2-dimethylpropionyl chloride distilled over calcium hydride before use,† is slowly added to the stirred solution. Although the reaction is usually complete after 24 h, its progress should be followed by NMR spectroscopy‡ in order to ensure

*Starting materials for the corresponding adamant-1-yl derivative are lithium bis(trimethylsilyl)-phosphide·2tetrahydrofuran and adamantoyl chloride.[8]

†This purification is necessary to remove traces of hydrogen chloride that otherwise would catalyze a rapid formation of tris(2,2-dimethylpropionyl)phosphine.[7]

‡Since the ^1H chemical shift values depend strongly on the solvent used, the compounds tri(trimethylsilyl)phosphine (I) and [2,2-dimethyl-1-(trimethylsiloxy)propylidene] (trimethylsilyl)phosphine (II) can best be identified by their $^3J_{P-H}$ coupling constants (I: 4.4 cps; II: 3.8 cps), or by their $\delta_{(^{31}P)}$ values (I: −251; II: +120).

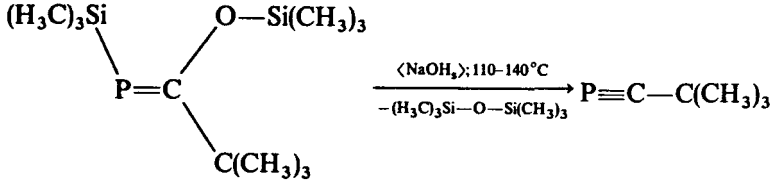
complete consumption of tris(trimethylsilyl)phosphine and to avoid further substitution.* After removing the volatile compounds under reduced pressure, the residual yellow alkylidenephosphine is purified by vacuum distillation. Bp 45–48 °C/10^{-3} mbar. Yield: 47.2 g (90%).

Anal. Calcd. for $C_{11}H_{27}OSi_2P$: Si, 21.4; P, 11.8. Found: Si, 21.5; P, 11.7.

Properties

[2,2-Dimethyl-1-(trimethylsiloxy)propylidene](trimethylsilyl)phosphine is a yellow viscous liquid. Characteristic NMR data for a solution in benzene are $(H_3C)_3C$ $\delta_{(^1H)}$ 1.25, $^4J_{P-H} = 1.5$; $(H_3C)_3Si-O$ $\delta_{(^1H)}$ 0.27; $(H_3C)_3Si-P$ $\delta_{(^1H)}$ 0.31, $^3J_{P-H} = 3.8$ cps; $\delta_{(^{31}P)}$ + 120. Substitution of another trimethylsilyl group by the 2,2-dimethylpropionyl moiety leads to (2,2-dimethylpropionyl)-[2,2-dimethyl-1-(trimethylsiloxy)propylidene]phosphine, which is the starting material for the keto–enol isomeric bis(2,2-dimethylpropionyl)-phosphine,[9] whereas reaction with alcohols gives (2,2-dimethylpropionyl)-phosphine.[10]

B. (2,2-DIMETHYLPROPYLIDYNE)PHOSPHINE[1,11]



■ **Caution.** *[2,2-Dimethyl-1-(trimethylsiloxy)propylidene](trimethylsilyl)phosphine is extremely sensitive to moisture and ignites in air. Therefore, all procedures must be carried out under an atmosphere of dry argon in a well-ventilated fume hood.*

Procedure

The apparatus (Fig. 1) consists of a two-necked 250-mL flask, one neck of which is equipped with a 100-mL pressure equalizing dropping funnel and a stopcock connected to the argon–vacuum supply, while the other neck is connected to a 200-mL cooling trap *via* a bent glass tube.† After adding

*The checkers report reaction times of 6 to 7 h using cyclohexane as the solvent and heating under reflux.

†Instead of a bent glass tube the checkers used a reflux condenser with running water.

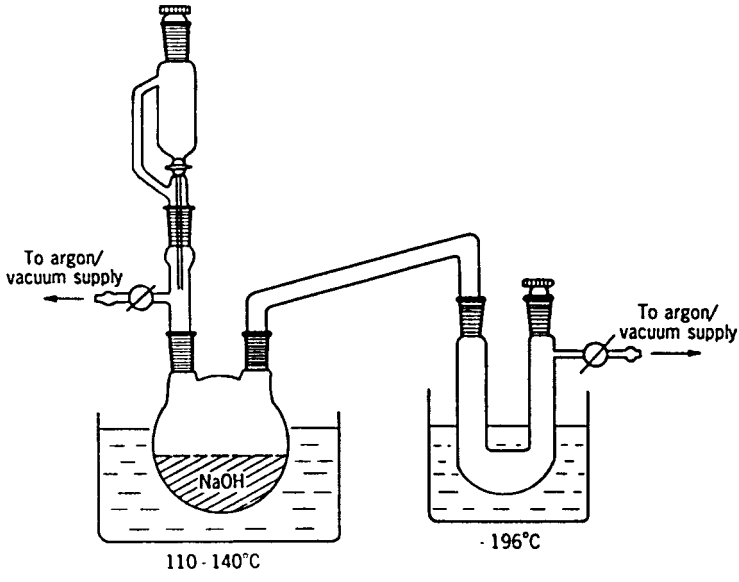


Fig. 1. Apparatus for preparing (2,2-dimethylpropylidyne)phosphine.

50.0 g (0.19 mol) of [2,2-dimethyl-1-(trimethylsiloxy)propylidene](trimethylsilyl)phosphine to the dropping funnel and ~10 g of granular sodium hydroxide to the 250-mL flask, the pressure within the apparatus is reduced to ~1 mbar, and the catalyst is heated to 110–140 °C with an oil bath. The alkylidenephosphine is then added very slowly over a period of 2 h in order to achieve a complete elimination of hexamethyldisiloxane. All volatile compounds are collected at −196 °C and separated later by fractional distillation under normal pressure.* Bp 52–57 °C. Yield after distillation: 14.0 g (74%).

Anal. Calcd. for C_5H_9P: C, 60.0; H, 9.1; P, 30.9. Found: C, 60.2; H, 9.0; P, 30.3.

Properties

(2,2-Dimethylpropylidyne)phosphine is a fairly volatile compound that is scarcely oxidized by air. Characteristic IR[1,12] and NMR data[1] are $\tilde{\nu}_{C\equiv P}$ 1533 cm^{-1}; $\delta_{(^1H)}$ 1.15, $^4J_{P-H} = 0.9$ cps; $\delta_{(^{31}P)}$ −69. Its chemical properties have recently been summarized.[2,13]

*Because of its high vapor pressure at room temperature, the distillate should be cooled with an ice bath.

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