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51. LITHIUM DIPHENYLPHOSPHIDE AND DIPHENYL(TRIMETHYLSILYL)PHOSPHINE

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A previous description of the synthesis of $(CH_3)_3SiP(C_6H_5)_2$ in *Inorganic Syntheses*[1] involves the initial preparation of sodium diphenylphosphide from diphenylphosphinous chloride. This method of preparation of the diphenylphosphide anion requires rigorous conditions and long reaction times. At least two other easier methods of preparation of the diphenylphosphide anion (lithium counterion) are known. One synthesis uses diphenylphosphine and *n*-butyllithium[2] as reactants, whereas the second uses triphenylphosphine and elemental lithium.[3,4] The second method is described here.

The phosphorus-carbon bond of triphenylphosphine is easily cleaved by lithium in THF (tetrahydrofuran) at room temperature. The phenyllithium which is also formed in this reaction is destroyed *in situ* by allowing it to react with 2-chloro-2-methylpropane. Isobutylene gas is given off and the diphenylphosphide ion is then allowed to react with chlorotrimethylsilane. The product, diphenyl(trimethylsilyl)phosphine, is formed in 80% yield. The diphenylphosphide ion is usually formed in 85–95% yield, based on the lithium consumed.

■ **Caution.** *All phosphines are toxic. The diphenylphosphide ion and silylphosphine are very sensitive to oxygen and moisture. All operations involving these materials should be carried out in an inert atmosphere and in a good hood. Any excess lithium metal should be destroyed with* 1-*propanol in an inert atmosphere. The tetrahydrofuran* (THF) *should be handled and dried carefully as previously described.*[5] (See also Synthesis 1 of this volume for dangers involved in drying THF.)

A. LITHIUM DIPHENYLPHOSPHIDE

$$(C_6H_5)_3P + 2Li \xrightarrow{THF} (C_6H_5)_2PLi + C_6H_5Li$$

$$C_6H_5Li + (CH_3)_3CCl \xrightarrow{THF} C_6H_6 + LiCl + (CH_3)_2C{=}CH_2$$

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Procedure

A clean, dry, 100-mL, two-necked, round-bottomed flask is set up with a reflux condenser (air-cooled) in a nitrogen-filled glove bag. To the second neck, a septum is attached. Twenty-five milliliters of freshly-dried THF and 10.5 g (0.04 mol) of triphenylphosphine are added to the flask, which contains a Teflon-coated magnetic stirring bar. Lithium metal (0.55 g, 0.08 mol) from which oil has been cleaned, is scraped, cut, and pressed into flat rods and is added to the THF-phosphine solution. After the solution is stirred, a red color forms which indicates formation of the diphenylphosphide ion. The air-cooled condenser is used because the heat liberated by this reaction causes the solvent to reflux. Within 2 hr the reaction is 85–95% complete, based on unreacted lithium, and the solution is dark-red. It has been observed that the smaller the amount of THF used, the faster the reaction proceeds and the greater is the rate of refluxing.

To the dark-red solution a sample of 2-chloro-2-methylpropane (3.7 g, 0.04 mol) is added slowly by means of a syringe. The formation of white precipitate and bubbling of solvent occurs. If the 2-chloro-2-methylpropane is added too quickly, the vigorous evolution of gas may cause difficulty. The dark-red color remains. This solution is then filtered in the glove bag, and the filtrate is placed into a pressure-equalized dropping funnel. The $(C_6H_5)_2PLi$ solution may now be used as a reagent for the introduction of the $(C_6H_5)_2P$ group into a variety of compounds.

B. DIPHENYL(TRIMETHYLSILYL)PHOSPHINE

$$(C_6H_5)_2PLi + (CH_3)_3SiCl \xrightarrow{\text{THF}} (CH_3)_3SiP(C_6H_5)_2 + LiCl$$

Procedure

The dropping funnel described in Sec. A, containing the $(C_6H_5)_2PLi$ solution, is attached to a 200-mL two-necked flask which contains chlorotrimethylsilane (4.32 g, 0.04 mol) in 25 mL of THF. The other neck contains an air-cooled condenser. The $(C_6H_5)_2PLi$ solution is added slowly, in a nitrogen-filled glove bag, to the chlorotrimethylsilane solution over a period of a half-hour. A white precipitate forms together with a clear or slightly yellow-colored solution. This mixture is filtered and washed with THF in the nitrogen-filled glove bag. The solvent is then removed by distillation under an atmosphere of nitrogen, and the residual material is purified by distillation at 1 torr. The 8.3-g (80% yield) fraction collected has bp 126–127°/1 torr, n_D^{25} 1.600 (lit.,[6] bp 126–127°/1 torr, n_D^{20} 1.600). When the reaction is carried out on a 0.1-mole scale, similar yields are obtained.

Properties

The properties of $(CH_3)_3SiP(C_6H_5)_2$ have been described previously in *Inorganic Syntheses.*[1]

References

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52. PENTATHIAZYL, $[S_5N_5]^+$, SALTS

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The pentathiazyl ion, $[S_5N_5]^+$, is the first 14π-electron member of the series of "electron-rich" aromatic sulfur-nitrogen heterocycles.[1,2] The preparations of the related species $S_2N_2(6\pi)$, $S_3N_2Cl_2$ (containing the 6π pseudo-aromatic $[S_3N_2Cl]^+$ cation), and salts of $[S_4N_3]^+(10\pi)$ have been described[3,4] in earlier volumes of *Inorganic Syntheses.* The monocyclic structure of the $[S_5N_5]^+$ ion has been established by x-ray diffraction methods.[5,6]

Pentathiazyl salts can be prepared in high yield in thionyl chloride solution at room temperature by adding solid tetrasulfur tetranitride to a 1 : 3 mixture of trichlorocyclotrithiazene,‡ $(NSCl)_3$, and a chloride ion acceptor such as iron(III) chloride, aluminum trichloride or antimony(V) chloride.[7,8] The adducts, $(NSCl)_3\cdot 2FeCl_3$, $(NSCl)_3\cdot 2AlCl_3$, and $(NSCl)_3\cdot 3SbCl_5$, respectively, are first formed. The $(NSCl)_3\cdot 2MCl_3$ adduct and an equimolar excess of MCl_3, or alternatively the $(NSCl)_3\cdot 3SbCl_5$ adduct can be regarded

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‡ 2,4,6-trichloro-1,3,5,2,4,6-trithiatriazine