in vacuo, 370 mg. of product was obtained. It was further purified by recrystallization from a mixture of 3 ml. of methanol, 3 ml. of 2-propanol, and 5 drops of water, yielding 290 mg., m.p. 224–226° dec., $[\alpha]^{22}\mathrm{D}$ 0.00 (*c* 3, water). The compound was chromatographically homogeneous in three different solvent systems: (1) 2-propanol–water (75:25), (2) pyridine–acetone–ammonia (6 *N*) (45:30:25), and (3) 2-propanol–formic acid–water (8:1:1).

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Synthesis and Reactions of Anhydrous Lithium Cyanide[1]

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A new synthesis of anhydrous lithium cyanide is reported. Its reactivity is compared with that of silver cyanide. With organic halogen compounds it yields the normal cyano derivative. Its reactions with phenacyl bromide, diphenylchlorophosphine oxide and sulfide, and with diphenyldicyanosilane are described.

Anhydrous lithium cyanide has been found to be an effective reagent for replacing the chloro group by the cyano group in some compounds which do not react with silver cyanide. The latter reagent is usually employed for such replacements on halo phosphines.[2,3] However, it fails to react with diphenylchlorophosphine sulfide, diphenylchlorophosphine oxide, or diphenyldichlorosilane. Anhydrous lithium cyanide reacts readily with these compounds to give good yields of the cyano derivatives. This reactivity is not surprising in view of the good solubility of lithium cyanide in solvents of high dielectric constant, its low melting point, and the high charge density of the unhydrated lithium ion.

Anhydrous lithium cyanide is easily prepared in high purity and yield by the reaction of liquid hydrogen cyanide with *n*-butyllithium. Anhydrous lithium cyanide has been synthesized previously by the treatment of lithium foil with 50% hydrogen cyanide in benzene[4] and by the reaction of anhydrous hydrogen cyanide with an ether suspension of hydrated lithium hydroxide.[5]

The synthesis of diphenylcyanophosphine sulfide by the use of anhydrous lithium cyanide can serve to illustrate the greater reactivity of lithium cyanide than silver cyanide. The sulfide III was synthesized by the following two routes: (1) by the reaction of phosphorus thiochloride with diphenylcyanophosphine (II), and (2) by the reaction of anhydrous lithium cyanide with diphenylchlorophosphine sulfide (I).

$$\begin{tikzcd}
\mathrm{Ph_2PCl} \arrow[r, "\mathrm{AgCN}"] \arrow[d, "\mathrm{PSCl_3}"'] & \begin{array}{c}\mathrm{Ph_2PCN}\\ \mathrm{II}\end{array} \arrow[d, "\mathrm{PSCl_3}"] \\
\begin{array}{c}\mathrm{Ph_2P(S)Cl}\\ \mathrm{I}\end{array} \arrow[r, "\mathrm{LiCN}"] & \begin{array}{c}\mathrm{Ph_2P(S)CN}\\ \mathrm{III}\end{array}
\end{tikzcd}$$

The reaction of I with silver cyanide yielded only starting material. However, the reaction of anhydrous lithium cyanide with I at room temperature yielded III (70%). The recovered residue (26%) proved to be undistillable material of various degrees of polymerization. The synthesis of III can also be carried out, however, in high yield by the reaction of phosphorus thiochloride with II.

Neither potassium cyanide nor silver cyanide reacted with diphenylchlorophosphine oxide, only starting material being recovered. However, with lithium cyanide an undistillable solid product was obtained in 59% yield. This product gave the correct analysis for diphenylcyanophosphine oxide but is undoubtedly polymeric.

The greater reactivity of anhydrous lithium cyanide is illustrated again in its reaction with diphenyldichlorosilane. There was no reaction between silver cyanide and diphenyldichlorosilane in refluxing benzene overnight or at 160–185° for 6 hr. without solvent. Lithium cyanide and diphenyldichlorosilane in refluxing benzene gave diphenyldicyanosilane in 68% yield. Silver cyanide does react with diphenyldibromosilane to give diphenyldiisocyanosilane in 80% yield, as described by McBride.[6]

Lithium cyanide reacted readily with phenacyl bromide in dimethylformamide solution to form benzoylacetonitrile, indicating that it yields the cyano and not the isocyano derivative.

Experimental

Lithium Cyanide.—*n*-Butyllithium (64 g., 1.0 mole) in hexane (Foote Mineral Co.) was transferred by filter stick under nitrogen pressure into a 1-l. three-necked, round-bottomed flask fitted with a pressure-equalizing dropping funnel, a nitrogen inlet tube, and a cold finger trap cooled with trichloroethylene–Dry Ice to −14°. A solution of anhydrous hydrogen cyanide (26 g., 0.96 mole) in 32 ml. of dry benzene was added dropwise and with rapid stirring to the *n*-butyllithium at 0–5°. There was immediate precipitation of a white solid. After the addition was complete, the reaction mixture was stirred for an additional 15 min. The contents of the flask were rapidly transferred under nitrogen to a 500 ml. filter apparatus equipped with a large coarse fritted disk and a 40–50 ground glass joint to facilitate pouring from the reaction flask under dry nitrogen. The white solid was washed four times with dry benzene and four times with petroleum ether (b.p. 30–60°) and dried under vacuum at 100–110° to yield 33.1 g. (quantitative yield), m.p. 161–162° (lit.[4] m.p. 160°).

Benzylacetonitrile.—Lithium cyanide and phenacyl bromide in acetonitrile or in dimethylformamide yielded benzoylacetonitrile, m.p. 80.5–80.7°. By vapor phase chromatography the product

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(1) Presented at the XIXth International Congress of Pure and Applied Chemistry, London, July 10–17, 1963.

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(3) Plets, dissertation, Kazan, 1938. As cited by G. M. Kosolapoff "Organophosphorus Compounds," John Wiley and Sons, Inc., N. Y., 1950, pp. 49, 55.

(4) A. Perret and R. Perrot, *Helv. Chim. Acta*, **15**, 1165 (1932).

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was proved to be greater than 90% pure, showing that LiCN yielded the cyano and not the isocyano derivative.

Diphenylchlorophosphine Sulfide (I).—This compound was prepared in a manner analogous to those of Rattenbury[7] and Jansen.[8] Diphenylchlorophosphine (44 g., 0.2 mole, $n^{21}\mathrm{D}$ 1.6325) and phosphorous thiochloride (34 g., 0.2 mole) were heated at 125° until evolution of the phosphorous trichloride ceased. Distillation of the residual solution *in vacuo* yielded 48 g. (95%) of I, a clear colorless liquid, b.p. 152–155° (0.55 mm.), $n^{20}\mathrm{D}$ 1.6563 (lit.[9] b.p. 155–160° at 0.3 mm.).

Diphenylcyanophosphine Sulfide (III). A. By II and Phosphorus Thiochloride.—Diphenylcyanophosphine (II) was prepared by the reaction of silver cyanide with diphenylchlorophosphine according to the method of Plets.[3] The colorless liquid (94% yield, b.p. 187–188° at 13.5 mm., $n^{20}\mathrm{D}$ 1.6205, d^{25}_{4} 1.1198) had elemental analyses in excellent agreement with the theoretical values. It did not solidify on standing (lit.[3] b.p. 170–175° at 15 mm., m.p. 39–40°).

Diphenylcyanophosphine (63 g., 0.3 mole) and phosphorus thiochloride (51 g., 0.3 mole, b.p. 125°) were heated at 102° until the by-product, phosphorus trichloride (b.p. 76°, 94%), ceased to distil. Distillation under reduced pressure yielded 56.8 g. (70%) of III as a colorless liquid, b.p. 149–151° (0.25 mm.), $n^{20}\mathrm{D}$ 1.6414, d^{25}_{4} 1.2023. This liquid solidified upon standing to give a white solid, m.p. 50.0–50.2°.

Anal. Calcd. for $C_{13}H_{10}NPS$: C, 64.18; H, 4.14; N, 5.76; P, 12.73; S, 13.18. Found: C, 64.25; H, 4.31; N, 5.72; P, 12.97; S, 13.00.

In other runs, the distillation was carried out also at 214–216° (9 mm.) to give the pure product. The infrared spectrum of the compound is consistent with the structure. The CN peak is observed at 2180 cm.$^{-1}$.

B. By I and Lithium Cyanide.—Anhydrous lithium cyanide (6.6 g., 0.2 mole) was added in portions under nitrogen to a solution of diphenylchlorophosphine sulfide (50 g., 0.2 mole) in 50 ml. of dry benzene. There was no immediate heat effect. After standing overnight at room temperature, the deep brown reaction mixture was heated at reflux for 1 hr. and then filtered by coarse fritted disk under nitrogen pressure. The solid was washed with two small portions of benzene. The combined filtrate and benzene washings were concentrated to a small volume. Distillation under reduced pressure yielded 33.7 g. (70%) of a colorless liquid, b.p. 213–214° (8.6 mm.), $n^{20}\mathrm{D}$ 1.6393. The liquid solidified on standing to a white solid. The values for melting point, boiling point, index of refraction, and the infrared spectrum are the same as those of the compound prepared by reaction of II with phosphorus thiochloride.

The pot residue consisted of a nondistillable brown solid with an average molecular weight of 1360 and believed to be low molecular weight polymers of diphenylcyanophosphine sulfide.

Diphenylcyanophosphine Oxide.—Diphenylchlorophosphine oxide (23.6 g., 0.1 mole, b.p. 168–169° at 1.2 mm., $n^{20}\mathrm{D}$ 1.6112) and anhydrous lithium cyanide (3.3 g., 0.1 mole) in 30 ml. of dry benzene were heated at reflux overnight. The reaction mixture was processed in the same manner as above. Distillation under diminished pressure gave 5.6 g. of starting material and 13.9 (59%) of an undistillable brown residue, m.p. 60–70°. This is the compound in the polymeric form to which these nitriles are readily converted.

Anal. Calcd. for $C_{13}H_{10}NOP$: N, 6.17; P, 13.63. Found: N, 5.83; P, 13.52.

Diphenyldicyanosilane.—Diphenyldichlorosilane (25 g., 0.1 mole, b.p. 99–100° at 0.3 mm.) was added dropwise to a suspension of anhydrous lithium cyanide (6.8 g., 0.206 mole) in 100 ml. of dry benzene. There was no heat evolution. After being heated at reflux overnight, the reaction mixture was processed in the same manner as above. Distillation of the residual liquid yielded 15.8 g. (67.5%) of a clear, colorless liquid, b.p. 118–122° (0.28 mm.), $n^{20}\mathrm{D}$ 1.5636, d^{24}_{4} 1.1146. The liquid was redistilled to give a main fraction, b.p. 122° (0.24 mm.), $n^{20}\mathrm{D}$ 1.5626, d^{26}_{4} 1.1067 (lit.[6] b.p. 142° at 2 mm., m.p. 46–48°, $n^{30}\mathrm{D}$ 1.559932, d^{30}_{4} 1.090432).

Anal. Calcd. for $C_{14}H_{10}N_2Si$: C, 71.75; H, 4.31; N, 11.35. Found: C, 71.36; H, 4.56; N, 10.56.

The infrared spectrum showed a major peak at 2180 cm.$^{-1}$ and a minor peak at 2260 cm.$^{-1}$. Separation by v.p.c. yielded two nearly equal components with the same absorption spectra except for the relative intensities of these two bands. It is possible, but as yet not proven, that the compound contains both cyano and isocyano groups.

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[8] W. L. Jansen, U. S. Patent 2,662,917 (1953).

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Preparation, Characterization, and Reactions of Lithium and Sodium Tetraalkylboron Compounds

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Lithium and sodium tetraalkylboron compounds have been prepared by the reaction of alkyllithium and alkylsodium reagents with trialkylboranes. These tetraalkylboron compounds show extreme reactivity toward air and were therefore identified by the formation of stable tetramethylammonium and tetrabutylphosphonium derivatives. Unusual infrared and n.m.r. absorption peaks at 2750–2800 cm.$^{-1}$ and 10–10.5 p.p.m., respectively, were present in the spectra of the tetravalent boron compounds. It was shown that these peaks arise from methylene groups adjacent to negative boron atoms. The stability of lithium tetraalkylboron compounds and tetramethylammonium tetrabutylboron in water, acetic acid, and sodium hydroxide solutions was studied. Hydrolysis with 20% acetic acid results in a rapid loss of 1 mole of alkane followed by a slow hydrolysis of the resultant trialkylborane. Air oxidation of lithium tetrabutylboron in tetrahydrofuran at 35° yielded 48% 1-butanol and 3% *n*-butyraldehyde of the theoretical amounts along with a 15% recovery of *n*-butane. The possible routes to these oxidation products are discussed.

Although the synthesis and chemistry of tetraaryl or mixed tetraarylalkylboron compounds have received considerable study,[1] relatively little is known about purely aliphatic tetravalent boron compounds. Over 30 years ago, Thompson and Stevens[2] reported an unsuccessful attempt to prepare these compounds. Soon after this report Johnson and his co-workers[3] observed a positive reaction when they combined tributylborane and *n*-butyllithium. In 1940 Schlesinger and Brown[4] obtained a white solid from the reaction of equimolar amounts of ethyllithium and trimethylborane, to which they assigned the formula $LiC_2H_5{\cdot}B(CH_3)_3$. In the ensuing years Hurd[5] prepared lithium tetramethylboron, and Parsons and co-workers[6] prepared lithium

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