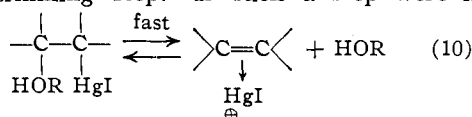


that reaction 10 follows reaction 7 and precedes the rate-determining step. If such a step were in-



cluded and were, in fact, fast and reversible, Ib would be converted rapidly to Ia in an aqueous solution, and the rates observed would have been the same for both compounds. In fact  $k_2$  for Ib is only about one-third of  $k_2$  for Ia.

The results discussed above show that the transition state in these reactions is composed of the substrate plus a proton. Beyond that its structure is not known. Neither is it known whether the rate-determining step leads directly to the products shown in eq. 8 or whether one or more intermediates intervene. These questions are currently under investigation in these laboratories and will be discussed when more evidence is available.

### Experimental

**Kinetic Procedure.**—All rate measurements were made by following the appearance of the  $\text{HgI}_2$  absorption at 2800 Å. with a Beckman DU spectrophotometer. The reaction mixtures were made up in volumetric flasks without the substrate and thermostated at  $25.00 \pm 0.05^\circ$  in a water-bath of conventional design. The substrate then was added in a small volume of stock solution. Part of the reaction mixture was transferred to a 1.00-cm. silica spectrophotometer cell and the cell was placed in a water-jacketed cell compartment for the course of the reaction. Water was pumped through the jackets from the bath mentioned above and the temperature in the cells was never found to vary from the bath temperature by more than  $0.1^\circ$ . The optical density was determined at convenient intervals over a range of 70–90% of its total change. Infinity points were determined by making a number of measurements after eight or more half-lives had passed.

Stock solutions of substrate were made up in methanol, so that the "aqueous" solutions referred to above actually contained 1–4% methanol. In view of the small difference between the rates in nearly pure water and those in 96% methanol, this small percentage of methanol was not thought to be significant, and  $k_2$  was shown to be invariant with changes in the percentage methanol between 1 and 4%. The 96% methanol solvents were made up in a 25-ml. volumetric flask, to which 1 ml. of water containing the requisite amount of acid had been added. The flask was then filled to the mark with methanolic stock solution of substrate plus pure, dry methanol.

**Materials.**—The preparation of solvents and standard acids has been described previously.<sup>8</sup> Compound Ia was prepared by the method of Hofmann and Sand,<sup>28</sup> m.p. 63–65°,

(28) K. A. Hofmann and J. Sand, *Ber.*, **33**, 1354 (1900).

and had an infrared spectrum characteristic of a secondary alcohol. Compound Ib does not seem to be previously known. It was prepared by essentially the method outlined by Wright<sup>29</sup> for the cyclohexene derivative, except that the olefin was passed into the reaction mixture as a gas; Ib is a liquid which freezes around  $0^\circ$  and could neither be recrystallized nor distilled. Fortunately, it seems to come out of the reaction mixture fairly pure. It had an infrared spectrum typical of an ether.

*Anal.* Calcd. for  $\text{C}_4\text{H}_9\text{OHgI}$ : C, 11.99; H, 2.26. Found: C, 11.51; H, 2.01.

**Ultraviolet Spectra.**—A standard solution of  $\text{HgI}_2$  in methanol was diluted 25-fold with water in order to obtain the spectrum of a solution of reliably known concentration. The spectrum of  $\text{HgI}^\oplus$  was obtained by mixing solutions containing one equivalent each of mercuric nitrate and sodium iodide.

**Products.**—In a typical determination of the volume of gas produced, 1.526 g. (0.00396 mole) of Ib was added to 50 ml. of water in a 500-ml. filter flask, which was then tightly stoppered with a dropping funnel passing up through the stopper. The side arm was connected to a gas buret through a short length of Tygon tubing and 1 ml. of 11 M  $\text{HClO}_4$  was added through the dropping funnel, which was then tightly closed. Fifty-four ml. of gas was collected at  $26^\circ$  and 740 mm. on shaking for about 15 minutes, and no further gas could be collected after 30 minutes of shaking. The liquid Ib was converted to red mercuric iodide during this time. The same procedure yielded 3 ml. of gas in the absence of Ib—probably due to  $\text{CO}_2$  evolution. The volume of propylene evolved was, therefore, 51 ml. Under these conditions only about 0.2% of the propylene would remain in the aqueous solution.<sup>30</sup> The total yield of gas was, therefore, 0.00203 mole.

When Ia was used, the solution was filtered to remove mercuric iodide, made basic with 2 M sodium hydroxide, and distilled. Ten ml. of this solution was treated with 1 ml. of 18.7 M sulfuric acid and 2.00 ml. of 0.102 M chromium(VI) oxide at  $62^\circ$  for 2.5 hours. No change in the visible spectrum of the chromium(VI) oxide could be detected spectroscopically. Under the same conditions, 10 ml. of  $1.32 \times 10^{-3}$  M isopropyl alcohol in water reduces 1.0 mole of chromium(VI) oxide to chromic ion, as determined spectroscopically. The spectrum of chromium(VI) oxide in these solutions was determined directly. The spectrum of the chromic ion was determined by heating 0.001 mole of isopropyl alcohol at  $62^\circ$  for 2.5 hours with  $2.04 \times 10^{-4}$  mole of chromic acid, 1 ml. of 18.7 M  $\text{H}_2\text{SO}_4$  and 12 ml. of water.

**Acknowledgment.**—The author is pleased to acknowledge the financial support of the National Science Foundation through grant No. N.S.F.-G5434 during part of the period when this work was in progress. He also wishes to thank Mrs. Olga Hamerston for the troublesome analysis of Ib.

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(29) G. F. Wright, *This Journal*, **57**, 1993 (1935).

(30) E. W. Washburn, ed., "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 260.

[CONTRIBUTION FROM STAMFORD LABORATORIES, RESEARCH DIVISION, AMERICAN CYANAMID CO.]

## The Cyanoethylation of Phosphine and Phenylphosphine

BY M. M. RAUHUT, I. HECHENBLEIKNER, HELEN A. CURRIER, F. C. SCHAEFER AND V. P. WYSTRACH

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Phosphine reacts with acrylonitrile at room temperature in the presence of strongly basic catalysts to give high yields of 2-cyanoethylphosphines. The primary, secondary or tertiary phosphine can be made the predominant product by choosing appropriate conditions. Phenylphosphine also reacts readily with acrylonitrile under these conditions to give a high yield of bis-(2-cyanoethyl)-phenylphosphine. A number of derivatives of tris-(2-cyanoethyl)-phosphine and bis-(2-cyanoethyl)-phenylphosphine have been prepared.

The reaction of active hydrogen compounds with acrylonitrile to produce derivatives containing a 2-cyanoethyl substituent is well known and has

been reviewed.<sup>1</sup> The cyanoethylation of the hy-

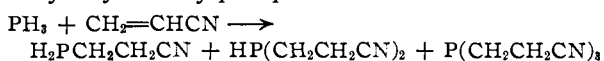
(1) H. A. Bruson, "Organic Reactions," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 79.

drudes of the Group V elements has been investigated in greatest detail with respect to derivatives of nitrogen. Ammonia and most aliphatic primary and secondary amines readily add to acrylonitrile in the absence of a catalyst, although a basic catalyst is useful with certain branched secondary amines.<sup>1</sup> The effective cyanoethylation of aryl amines and *t*-carbinamines requires the use of acidic catalyst<sup>1,2,3</sup> or copper salts.<sup>4,5</sup> The extent of substitution in these reactions can be controlled by proper choice of reaction conditions.

The cyanoethylation of methylarsine and several arylarsines has been investigated by Mann and co-workers<sup>2,6,7</sup> who found that, while the reaction was strongly catalyzed by sodium methoxide, the arylarsines reacted readily even in the absence of catalyst. Mann and Millar<sup>8</sup> have investigated the uncatalyzed cyanoethylation of phenylphosphine and diphenylphosphine at 130°. They reported that under their relatively vigorous conditions the addition of a trace of sodium methoxide appreciably decreased the yields of cyanoethylated products and caused a corresponding increase in tarry by-products.

We have found that phosphine and phenylphosphine are cyanoethylated readily in the presence of a strong base. Moreover, base catalysis is so effective that even with phosphine the reaction can be carried out conveniently at room temperature and atmospheric pressure. The best yields were obtained when acetonitrile in conjunction with a separate aqueous potassium hydroxide catalyst phase was employed as the reaction medium. Under these conditions the low reaction temperature and the presence of water minimized polymerization of the acrylonitrile and gave a clean reaction mixture.

The cyanoethylation of phosphine invariably gave mixtures of the primary, secondary and tertiary 2-cyanoethylphosphines.

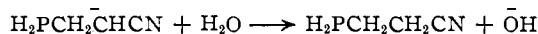
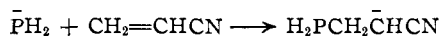
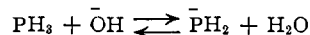


The degree of substitution could be controlled, however, by varying the ratio of phosphine to acrylonitrile present in the reaction mixture. Thus, tris-(2-cyanoethyl)-phosphine was prepared in 80% yield by adding phosphine to a mixture containing a slight excess of acrylonitrile, while bis-(2-cyanoethyl)-phosphine was prepared in 58 to 63% yields by adding acrylonitrile slowly to a mixture constantly saturated with phosphine. 2-Cyanoethylphosphine was prepared in 52% yield by carrying out the reaction in an autoclave under a phosphine pressure of 28 to 32 atmospheres.

Two strong organic bases, heptamethylbiguanide and Dowex-2 quaternary ammonium ion-exchange resin also catalyzed the reaction. However, compared to the aqueous potassium hydroxide

catalyst, heptamethylbiguanide tended to give less clean reaction mixtures, and Dowex-2 ion-exchange resin required a somewhat higher temperature.

Although the acidic character of phosphine is very slight,<sup>9</sup> it is probable that the reaction takes place by a Michael reaction mechanism.<sup>10</sup> The



phosphide ion has also been proposed as an intermediate in the base-catalyzed exchange of hydrogen between phosphine and deuterium oxide.<sup>9</sup>

The cyanoethylation of phosphine is not readily reversed. When tris-(2-cyanoethyl)-phosphine was refluxed with excess ethanol in the presence of heptamethylbiguanide all of the tertiary phosphine was recovered unchanged. Pyrolysis of tris-(2-cyanoethyl)-phosphine at 315° under nitrogen gave small amounts of white phosphorus and propionitrile, but the formation of acrylonitrile or bis-(2-cyanoethyl)-phosphine could not be detected.

Phenylphosphine, like phosphine, reacted readily with acrylonitrile in the presence of aqueous potassium hydroxide and acetonitrile to give an 82% yield of bis-(2-cyanoethyl)-phenylphosphine.

2-Cyanoethylphosphine and bis-(2-cyanoethyl)-phosphine are colorless liquids with characteristic phosphine-like odors. They are distillable under vacuum without decomposition. Bis-(2-cyanoethyl)-phosphine gave no evidence of disproportionation to primary and tertiary phosphines, a reaction which has been suggested<sup>11</sup> to occur with secondary phosphines. Both 2-cyanoethylphosphine and bis-(2-cyanoethyl)-phosphine are rapidly oxidized by air.<sup>12</sup> Tris-(2-cyanoethyl)-phosphine is a white crystalline solid and is not oxidized by air even at elevated temperatures. It is only weakly basic ( $K_b = 10^{-13}$ ).<sup>13</sup> In these respects tris-(2-cyanoethyl)-phosphine resembles triphenylphosphine,<sup>14</sup> but differs from other trialkyl phosphines which, in general, are easily oxidized by air<sup>15</sup> and have a more pronounced basic character.<sup>16</sup> This resistance to oxidation and weak basicity are indicative of a decreased electron density around the phosphorus atom, which evidently results from the inductive effect of the cyano groups.

In other respects tris-(2-cyanoethyl)-phosphine was found to undergo reactions typical of tertiary phosphines, and a number of derivatives were prepared as shown in the accompanying chart.

(9) R. E. Weston, Jr. and J. Bigeleisen, *THIS JOURNAL*, **76**, 3074 (1954).

(10) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 691.

(11) G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 14.

(12) The chemistry of these compounds will be discussed in detail in forthcoming communications.

(13) C. A. Streuli, unpublished results.

(14) A. Michaelis and L. Gleichmann, *Ber.*, **15**, 801 (1882).

(15) A. W. Hofmann and A. Cahours, *J. Chem. Soc.*, **11**, 56 (1858);

W. C. Davies, P. L. Pearse and W. J. Jones, *ibid.*, 1262 (1929).

(16) H. C. Brown, *THIS JOURNAL*, **67**, 503 (1945).

(2) R. C. Cookson and F. G. Mann, *J. Chem. Soc.*, 67 (1949).

(3) J. T. Brauholtz and F. G. Mann, *ibid.*, 3046 (1952); L. S. Luskin, *et al.*, *THIS JOURNAL*, **78**, 4042 (1956).

(4) S. A. Heininger, *J. Org. Chem.*, **22**, 1213 (1957).

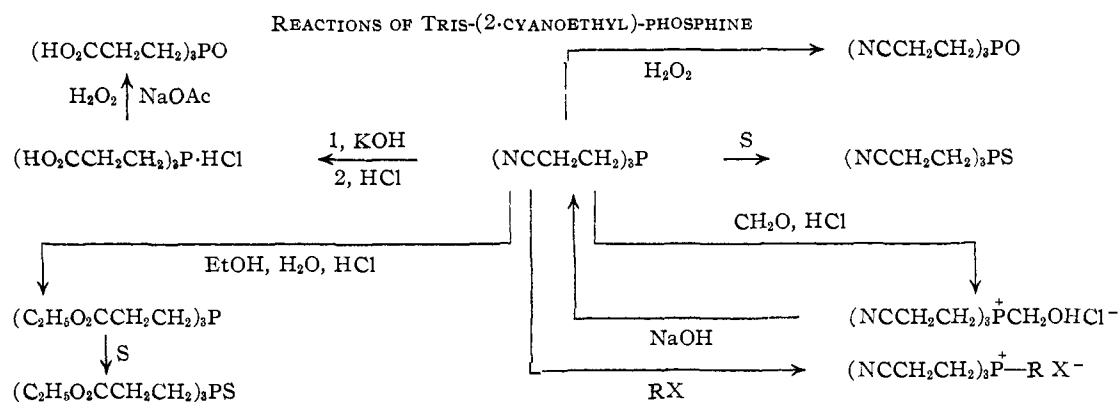
(5) Cf. P. A. Smith, Tung-yin Yu, *THIS JOURNAL*, **74**, 1098 (1952);

J. T. Brauholtz and F. G. Mann, *J. Chem. Soc.*, 1817 (1953); J. T. Brauholtz and F. G. Mann, *ibid.*, 651 (1954).

(6) R. C. Cookson and F. G. Mann, *ibid.*, 618 (1947).

(7) F. G. Mann and A. J. Wilkinson, *ibid.*, 3336 (1957).

(8) F. G. Mann and I. T. Millar, *ibid.*, 4453 (1952).



Oxidation of bis-(2-cyanoethyl)-phenylphosphine with hydrogen peroxide in acetic acid gave bis-(2-cyanoethyl)-phenylphosphine oxide in 91% yield. The oxide could be recrystallized easily from isopropyl alcohol and thus was apparently different from the highly soluble product Mann and Millar<sup>8</sup> obtained by the oxidation of bis-(2-cyanoethyl)-phenylphosphine with hydrogen peroxide in acetone. Hydrolysis of the oxide gave a 90% yield of bis-(2-carboxyethyl)-phenylphosphine oxide.

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#### Experimental Section<sup>17</sup>

**Materials.**—Aluminum phosphide was supplied by the Hooker Electrochemical Co. Phosphine for atmospheric pressure experiments was generated as needed by the reaction of aluminum phosphide with water. For superatmospheric pressure experiments, liquid phosphine in stainless steel cylinders was obtained from Rocky Mountain Research, Inc., and used without further purification. Phenylphosphine was prepared by the method of Mann and Millar.<sup>18</sup> Heptamethylbiguanide<sup>19</sup> was prepared by the alkylation of hexamethylbiguanide<sup>20</sup> with dimethyl sulfate. Other starting materials were obtained from commercial sources.

**Apparatus for the Addition of Phosphine to Acrylonitrile at Atmospheric Pressure.**—Caution: Phosphine is a highly poisonous and flammable gas. The apparatus consisted of a phosphine generator (a 3-liter, three-neck flask fitted with a one-liter pressure-equalized dropping funnel, a gas-tight mechanical stirrer, and a 40-cm. bulb reflux condenser) and a reactor (a 5-liter, three-neck Morton flask fitted with a one-liter pressure-equalized dropping funnel, a gas-tight mechanical stirrer, a thermometer, and a gas inlet-outlet adapter whose inlet extended nearly to the bottom of the flask). The generator condenser outlet was connected with rubber tubing by way of a bubbler and a trap to the gas inlet of the reactor. The gas outlet was connected by way of a trap to a terminal bubbler (a 60-cm. vacuum trap, three-quarters filled with water), and the exit of the terminal bubbler led directly to the hood exhaust. All fittings and connections were wired before phosphine generation was begun.

**Bis-(2-cyanoethyl)-phosphine.**—One liter of dioxane<sup>21</sup> and 585 g. (10 moles) of aluminum phosphide were charged into

the phosphine generator flask and one liter of water was placed in the generator dropping funnel. In the reactor flask were placed 1500 ml. of acetonitrile and 300 ml. of 10 N aqueous potassium hydroxide solution. One liter (604 g., 15 moles) of acrylonitrile was placed in the reactor dropping funnel.

The entire system was swept with dry nitrogen for 20 minutes while the slurry in the generator was warmed to about 50°. The nitrogen sweep then was discontinued and phosphine generation was begun by the dropwise addition of water to the generator. Rapid stirring was begun in the reactor, and a rapid stream of phosphine was passed through the system for 10 minutes. Dropwise addition of acrylonitrile was begun then at such a rate that the addition was complete in 3.5 hours.<sup>22</sup> Absorption of phosphine began immediately and the rate of phosphine generation was adjusted so that 2 to 5 bubbles per minute passed through the terminal bubbler. The temperature in the reactor rose and was maintained at 30–35° by means of an ice-bath. The generator became hot but cooling was not necessary. Absorption of phosphine stopped within two minutes after the addition of acrylonitrile was complete.

When the aluminum phosphide was exhausted the system was swept with nitrogen, and the reaction mixture was transferred under nitrogen to a separatory funnel. The organic phase was separated, washed with three 100-ml. portions of saturated sodium chloride solution, and dried with anhydrous sodium sulfate. The solvent was removed at the water-pump, and the residue was distilled to obtain 84 g. (6%) of 2-cyanoethylphosphine, b.p. 54–55° (9 mm.),  $n_D^{20}$  1.4831, and 591 g. (56%) of bis-(2-cyanoethyl)-phosphine, b.p. 157–159° (0.3 mm.),  $n_D^{20}$  1.5070.

*Anal.* Calcd. for  $\text{C}_2\text{H}_5\text{NP}$ : C, 41.38; H, 6.95; P, 35.58. Found: C, 41.20; H, 7.16; P, 35.63. Calcd. for  $\text{C}_6\text{H}_9\text{N}_2\text{P}$ : C, 51.43; H, 6.47; P, 22.11. Found: C, 51.91; H, 6.65; P, 21.50.

The warm distillation residue was poured into ice-water with vigorous stirring. The resulting solid was collected on a filter, and washed with cold methanol to obtain 276 g. (28%) of crude tris-(2-cyanoethyl)-phosphine, m.p. 88–93°. Recrystallization from 50% aqueous acetic acid provided white needles, m.p. 98–99°.

*Anal.* Calcd. for  $\text{C}_6\text{H}_{12}\text{N}_3\text{P}$ : N, 21.77; P, 16.06. Found: N, 21.92; P, 16.07.

In a similar experiment excess phosphine and 80.6 g. (1.5 moles) of acrylonitrile were added during 2 hours to a stirred suspension of 20 g. of moist, basic Dowex-2 ion-exchange resin in 150 ml. of acetonitrile while the temperature was maintained at 45–50° by cooling. The catalyst was removed by filtration and the filtrate was distilled to obtain 6.5 g. (5%) of 2-cyanoethylphosphine, 46 g. (44%) of bis-(2-cyanoethyl)-phosphine and 24 g. (25%) of tris-(2-cyanoethyl)-phosphine.

**Tris-(2-cyanoethyl)-phosphine. A. Potassium Hydroxide Catalyst.**—The procedure was essentially the same as that described above. Phosphine, generated from 116 g. (2.0 moles) of aluminum phosphide slurried in 200 ml. of

(17) Boiling points and melting points are uncorrected.

(18) F. G. Mann and I. T. Müller, *J. Chem. Soc.*, 3039 (1952).

(19) I. Hechenbleikner and F. C. Schaefer, unpublished work.

(20) I. Hechenbleikner, U. S. Patent 2,768,204 (October 23, 1956); I. Hechenbleikner and D. W. Kaiser, U. S. Patent 2,768,205 (October 23, 1956).

(21) The dimethyl ether of ethylene glycol was also used to provide a stirrable slurry, but when the monomethyl ether was used, considerable evolution of hydrogen was observed.

(22) More rapid addition of acrylonitrile seriously decreased the yield of bis-(2-cyanoethyl)-phosphine and caused a corresponding increase in the yield of tris-(2-cyanoethyl)-phosphine. In reactions carried out at one-tenth the above scale the rate of addition was not critical.

dioxane, was added simultaneously with 282 g. (5.3 moles) of acrylonitrile to a well stirred mixture of 350 ml. of acetonitrile and 75 ml. of 10 *N* aqueous potassium hydroxide during 1.5 hours. The reaction mixture was stirred rapidly under nitrogen for an additional hour and poured into ice-water. The solid was collected, washed with water and cold methanol, and air-dried to obtain 280 g. (80%) of tris-(2-cyanoethyl)-phosphine, m.p. 90–94°.

**B. Heptamethylbiguanide Catalyst.**—A conventional Parr low-pressure hydrogenation apparatus was modified by providing it with a sight glass to permit the controlled addition of a liquid reactant to the reaction bottle while under pressure. The Parr tank was evacuated and then charged to a pressure of 3.6 atmospheres with phosphine. In the reaction bottle was placed a solution of 0.5 g. of heptamethylbiguanide<sup>16</sup> in 100 ml. of acetonitrile. A solution of 27.0 g. (0.51 mole) of acrylonitrile in 30 ml. of acetonitrile was placed in the sight glass. The reaction bottle was evacuated and charged with phosphine. The shaker was started and the acrylonitrile solution was added gradually under nitrogen pressure over a period of 3 hours. No evolution of heat was observed. The reaction mixture was shaken for an additional 30 minutes, after which the pressure remained constant at 2.6 atmospheres. The reaction bottle was evacuated, and then filled with nitrogen. The reaction mixture was transferred to a round-bottomed flask, and the solvent was evaporated under reduced pressure. The liquid residue was treated with 15 g. of acrylonitrile, and a vigorous exothermic reaction resulted. The excess acrylonitrile was evaporated under reduced pressure, and the residue was recrystallized from water to obtain 15.0 g. of tris-(2-cyanoethyl)-phosphine, m.p. 94–96°.

**2-Cyanoethylphosphine.**—Into a 3-liter stirred autoclave, equipped with a water jacket for cooling, were placed 1050 ml. of acetonitrile and 210 ml. of 10 *N* potassium hydroxide solution. The vessel was evacuated, rapid stirring was begun and phosphine was added to a pressure of 32 atmospheres. Acrylonitrile (560 g., 10.5 moles) then was added gradually during 250 minutes. The temperature was maintained at 28–30°, and the phosphine pressure was maintained between 28 and 32 atmospheres by recharging when necessary. The total weight of phosphine added to the reactor was 733 g. When all of the acrylonitrile had been added, the reaction mixture was stirred an additional 15 minutes, and then most of the excess phosphine was vented into a storage bomb cooled in an acetone–Dry Ice mixture. The recovered phosphine (382 g.) was essentially pure. When the pressure in the reactor had dropped to 5 atmospheres, prepurified nitrogen was charged to a pressure of 69 atmospheres, and the reaction vessel was vented into an efficient exhaust. This cycle was repeated twice to ensure removal of phosphine. Finally the reactor was evacuated and held at a pressure of 20 mm. for 10 minutes. The organic phase was separated from the reaction mixture, washed with saturated sodium chloride solution, and distilled to obtain 475 g. (52%) of 2-cyanoethylphosphine and 86 g. (12%) of bis-(2-cyanoethyl)-phosphine.

**Bis-(2-cyanoethyl)-phenylphosphine.**—Twenty-four grams (0.46 mole) of acrylonitrile was added dropwise during 15 minutes to a rapidly stirred mixture of 25.0 g. (0.23 mole) of phenylphosphine, 25 ml. of acetonitrile and 5.0 ml. of 10 *N* aqueous potassium hydroxide under nitrogen. A vigorous reaction was observed during the first half of the addition, but only a mild reaction occurred during the second half. The temperature was maintained at 25–30° by cooling in an ice-bath. After the addition, the reaction mixture was stirred for 2.5 hours. The organic layer was separated, washed with three 10-ml. portions of saturated sodium chloride solution, dried with anhydrous sodium sulfate, and distilled. The major portion, b.p. 215–223° (0.2 mm.), crystallized on standing to give 38.2 g. (77%) of bis-(2-cyanoethyl)-phenylphosphine, m.p. 73–74° (lit.<sup>8</sup> m.p. 72–73°). A small forerun was recrystallized from ethanol to obtain an additional 2.5 g. (5%) of product, m.p. 72–73°.

**Attempted Reaction of Tris-(2-cyanoethyl)-phosphine with Ethanol.**—A solution of 9.0 g. of tris-(2-cyanoethyl)-phosphine and 1.0 g. of heptamethylbiguanide in 50 ml. of absolute ethanol was heated under reflux for 3.5 hours. The solution was cooled in an ice-bath and filtered to obtain the starting phosphine, m.p. 96–98°, quantitatively.

**Attempted Air Oxidation of Tris-(2-cyanoethyl)-phosphine.**—One gram of the phosphine was spread in a thin

layer and heated in air at 200–210° for one hour. When cool, the melt crystallized to a yellow solid, m.p. 81–92°. The infrared spectrum was essentially the same as that of the starting material but indicated that carbonyl impurities were present. Absorption bands corresponding to tris-(2-cyanoethyl)-phosphine oxide were absent.

**Tris-(2-cyanoethyl)-phosphine Oxide.**—Ninety-seven grams (0.5 mole) of tris-(2-cyanoethyl)-phosphine was dissolved in 250 ml. of glacial acetic acid by warming to 55°. A solution of 53 g. (0.5 mole) of 32% aqueous hydrogen peroxide in 25 ml. of glacial acetic acid was added dropwise with stirring while the temperature was maintained at 50–55° by means of an ice-bath. The solution was stirred at 50° for an additional 30 minutes and concentrated to about 100 ml. at the water-pump. Acetone (100 ml.) was added, and the precipitated solid was collected on a filter and air-dried to obtain 90 g. (86%) of the oxide, m.p. 172–173°. Recrystallization from aqueous isopropyl alcohol did not change the melting point.

*Anal.* Calcd. for C<sub>6</sub>H<sub>12</sub>N<sub>3</sub>PO: C, 51.66; H, 5.78. Found: C, 51.68; H, 5.81.

**Tris-(2-cyanoethyl)-phosphine Sulfide.**—A mixture of 19.3 g. (0.1 mole) of tris-(2-cyanoethyl)-phosphine, 3.5 g. (0.11 mole) of sulfur and 100 ml. of benzene was heated under reflux with stirring for 1 hour. The product was filtered from the cool reaction mixture and recrystallized from 600 ml. of water to obtain 17 g. (76%) of the sulfide, m.p. 141–142°.

*Anal.* Calcd. for C<sub>6</sub>H<sub>12</sub>N<sub>3</sub>PS: C, 47.14; H, 5.27; N, 18.34; P, 13.51; S, 15.72. Found: C, 47.27; H, 5.61; N, 18.37; P, 13.44; S, 15.99.

**Tris-(2-carboxyethyl)-phosphine Hydrochloride.**—Tris-(2-cyanoethyl)-phosphine (386 g., 2.0 moles) was added with stirring to Claisen alkali, prepared by diluting a solution of 220 g. of potassium hydroxide in 160 ml. of water to 625 ml. with methanol. The mixture was warmed on the steam-bath, and a vigorous reaction occurred. When the mixture had cooled, an additional 220 g. of potassium hydroxide in 160 ml. of water and 100 ml. of methanol was added. The reaction mixture was warmed on the steam-bath and again a vigorous exothermic reaction occurred. The reaction mixture boiled spontaneously for an hour and then was refluxed on the steam-bath for 3 additional hours. Nitrogen was then passed through the solution with continued stirring and refluxing for 8 hours. The solution was cooled and made acidic with concentrated hydrochloric acid. The potassium chloride was removed and the filtrate was concentrated on the steam-bath under reduced pressure. The residue was extracted with boiling glacial acetic acid, and the extract when cool deposited 400 g. (70%) of the hydrochloride, m.p. 174–178°. Recrystallization from glacial acetic acid provided an analytical sample, m.p. 175–177°.

*Anal.* Calcd. for C<sub>6</sub>H<sub>16</sub>ClO<sub>3</sub>P: C, 37.70; H, 5.62; P, 10.80; Cl, 12.37. Found: C, 37.89; H, 5.64; P, 10.75; Cl, 12.16.

The potentiometric titration curve of the hydrochloride showed two breaks occurring at 3 and 4 equivalents of sodium hydroxide. The first break corresponds to the formation of a zwitterion, (NaO<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>PHCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub><sup>⊖</sup>.

**Tris-(2-carboxyethyl)-phosphine Oxide.**—A solution of 10 g. (0.1 mole) of 34% hydrogen peroxide in 10 ml. of water was added dropwise to a stirred solution of 28.7 g. (0.1 mole) of tris-(2-carboxyethyl)-phosphine hydrochloride and 8.2 g. (0.1 mole) of sodium acetate in 50 ml. of water. The temperature was held at 55–60° by cooling. The resulting solution was allowed to cool to 25° and, after a negative starch-iodide test, was evaporated to dryness under reduced pressure. The residue was extracted with 50 ml. of hot glacial acetic acid. Methyl isobutyl ketone (100 ml.) was added to the extract and the precipitated solid was collected to obtain 25.1 g. (94.5%) of the oxide, m.p. 151–153°. Ten grams recrystallized from isopropyl alcohol furnished 7.9 g. of the pure compound, m.p. 155–156°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>16</sub>O<sub>7</sub>P: C, 40.61; H, 5.68; P, 11.63. Found: C, 40.71; H, 5.44; P, 11.43.

**Tris-(2-carbomethoxyethyl)-phosphine.**—A suspension of 20.0 g. (0.10 mole) of tris-(2-cyanoethyl)-phosphine in 70 ml. of anhydrous ethanol and 5.0 ml. (0.28 mole) of water was saturated with dry hydrogen chloride while the tem-

perature was maintained below 50° by cooling. The mixture was allowed to stand overnight and filtered to remove ammonium chloride. The filtrate was concentrated under reduced pressure, and the residual slush was dissolved in 100 ml. of water. The solution was made alkaline with 40% sodium hydroxide solution and the resulting mixture was extracted with three 40-ml. portions of chloroform. The combined extracts were washed with water, dried with anhydrous sodium sulfate and distilled under reduced pressure to obtain 16.0 g. (47%) of the ester, b.p. 193–194° (1 mm.),  $n_D^{25}$  1.4748.

*Anal.* Calcd. for  $C_{18}H_{27}O_6P$ : C, 53.88; H, 8.14. Found: C, 53.92; H, 8.38.

**Tris-(2-carbomethoxyethyl)-phosphine Sulfide.**—Under a nitrogen atmosphere 5.0 g. of tris-(2-carbomethoxyethyl)-phosphine was added in one portion to a stirred mixture of 0.5 g. of sulfur and 30 ml. of benzene. After the exothermic reaction had subsided, the mixture was refluxed for 30 minutes and then distilled under reduced pressure to obtain the sulfide, a pale yellow oil, b.p. 214° (1 mm.),  $n_D^{25}$  1.5005.

*Anal.* Calcd. for  $C_{18}H_{27}O_6PS$ : C, 49.16; H, 7.42. Found: C, 48.89; H, 7.41.

**Bis-(2-cyanoethyl)-phenylphosphine Oxide.**—To a solution of 8.0 g. (0.037 mole) of bis-(2-cyanoethyl)-phenylphosphine in 20 ml. of acetic acid, preheated to 60°, was added dropwise during one hour 4.2 g. (0.037 mole) of 30% hydrogen peroxide solution. The heat of the reaction maintained the temperature between 60 and 70° during the addition. The reaction mixture then was heated at 75° for 15 minutes, treated with Darco, and heated at 100° for an additional 15 minutes. Filter aid was added, and the mixture was filtered. Evaporation of the solvent under reduced pressure gave a white crystalline solid. Recrystallization from isopropyl alcohol provided 7.8 g. (91%) of bis-(2-cyanoethyl)-phenylphosphine oxide, m.p. 108–109°.

*Anal.* Calcd. for  $C_{12}H_{12}N_2OP$ : C, 62.07; H, 5.64; P, 13.34. Found: C, 61.92; H, 5.53; P, 13.55.

**Bis-(2-carboxyethyl)-phenylphosphine Oxide.**—Bis-(2-cyanoethyl)-phenylphosphine oxide (5.6 g., 0.024 mole) was added to Claisen alkali, made by adding 16 ml. of methanol to a cool solution of 5.4 g. (0.096 mole) of potassium hydroxide in 4 ml. of water. The reaction mixture was heated under reflux for 5.5 hours. It was then neutralized with dilute hydrochloric acid and concentrated under reduced pressure to obtain 5.8 g. (90%) of bis-(2-carboxyethyl)-phenylphosphine oxide, m.p. 201–204°. Recrystallization from methanol provided an analytical sample, m.p. 199–202°.

*Anal.* Calcd. for  $C_{12}H_{12}O_6P$ : C, 53.34; H, 5.60; P, 11.46. Found: C, 53.01; H, 5.82; P, 11.15.

**Methyltris-(2-cyanoethyl)-phosphonium Iodide.**—A mixture of 1.0 g. of tris-(2-cyanoethyl)-phosphine and 1.0 g. of

methyl iodide was warmed on the steam-bath for 15 minutes. The product was washed onto a filter with ethanol and recrystallized twice from acetonitrile to obtain the iodide, m.p. 238–239°.

*Anal.* Calcd. for  $C_{10}H_{16}IN_3P$ : C, 35.83; H, 4.51. Found: C, 35.56; H, 4.63.

**Allyltris-(2-cyanoethyl)-phosphonium Chloride.**—A solution of 10.0 g. (0.052 mole) of tris-(2-cyanoethyl)-phosphine and 4.0 g. (0.052 mole) of allyl chloride in 25 ml. of dimethylformamide was heated under reflux for 3 hours. The solvent was evaporated under reduced pressure to give an oil which crystallized on treatment with acetone. The white solid was dissolved in acetic acid, and the solution was diluted with 3 volumes of acetone. While standing at 0° overnight the solution deposited white crystals, which after drying at 80° *in vacuo* melted at 135–136°.

*Anal.* Calcd. for  $C_{12}H_{17}ClN_3P$ : Cl, 13.14; P, 11.48. Found: Cl, 13.27; P, 11.28.

An aqueous solution of the chloride when treated with sodium picrate solution deposited a yellow solid, which after recrystallization from a mixture of ethanol and acetone melted at 126–127°.

*Anal.* Calcd. for  $C_{18}H_{19}N_6O_7P$ : C, 46.75; H, 4.14. Found: C, 46.56; H, 4.31.

**2,4-Dichlorobenzyltris-(2-cyanoethyl)-phosphonium Iodide.**—A solution of 5.0 g. (0.026 mole) of tris-(2-cyanoethyl)-phosphine and 5.0 g. (0.026 mole) of 2,4-dichlorobenzyl chloride in 25 ml. of dimethylformamide was heated under reflux for 2 hours, cooled and poured into 100 ml. of ether. The resulting oil was dissolved in water and treated with saturated potassium iodide solution. The crystalline iodide was collected and recrystallized from water to obtain 5.0 g. of white plates, m.p. 176–177°.

*Anal.* Calcd. for  $C_{16}H_{17}Cl_2IN_3P$ : I, 26.43. Found: I, 26.70.

**Hydroxymethyltris-(2-cyanoethyl)-phosphonium Chloride.**—To a solution of 19.3 g. (0.1 mole) of tris-(2-cyanoethyl)-phosphine in 25 ml. of concentrated hydrochloric acid was added portionwise with stirring 8.9 g. (0.11 mole) of 37% aqueous formaldehyde solution. The temperature rose to 50° during the addition. The solution was allowed to stand an additional 15 minutes and then was evaporated to dryness. The residue was recrystallized from acetic acid and dried at 80° *in vacuo* to obtain the product, m.p. 149–151°.

*Anal.* Calcd. for  $C_{10}H_{15}ClN_3OP$ : C, 46.24; H, 5.82; P, 11.92; N, 16.18. Found: C, 46.35; H, 6.03; P, 12.03; N, 16.11.

The product was soluble in water, but when an aqueous solution was treated with 5% sodium hydroxide solution the starting phosphine separated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

## Some Reactions of Silyllithium Compounds with Epoxides

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The addition of silylmetallic compounds to ethylene oxide, propylene oxide, cyclohexene oxide and styrene oxide has been found to give good yields of  $\beta$ -silylcarbinols. Some dehydration reactions of these carbinols have been studied. The reaction of triphenylsilyllithium with epibromohydrin and with epichlorohydrin was investigated.

A variety of silyl-substituted carbinols has been prepared recently using silylmetallic reagents. Triphenylsilyllithium (I) and methyl-diphenylsilyllithium have been found to cleave tetrahydrofuran with the formation of 4-silyl-substituted butanols.<sup>1,2</sup> Similarly, I reacted with trimethylene oxide to form 3-(triphenylsilyl)-propanol.<sup>2</sup> Various  $\alpha$ -

(1) D. Wittenberg and H. Gilman, *THIS JOURNAL*, **80**, 2677 (1958).

(2) D. Wittenberg, D. Aoki and H. Gilman, *ibid.*, **80**, 5933 (1958).

silylcarbinols have been prepared from the reaction of silyllithium or silylpotassium compounds with aliphatic aldehydes,<sup>3,4</sup> aliphatic ketones,<sup>5,6</sup> and with acid chlorides.<sup>4</sup>

(3) H. Gilman and T. C. Wu, *ibid.*, **76**, 2502 (1954).

(4) D. Wittenberg and H. Gilman, *ibid.*, **80**, 4529 (1958); also, unpublished studies by D. J. Peterson.

(5) A. G. Brook, *ibid.*, **80**, 1886 (1958).

(6) H. Gilman and G. D. Lichtenwalter, *ibid.*, **80**, 2680 (1958).