853. *The Cyanoethylation of Aryl Phosphines.*

By FREDERICK G. MANN and IAN T. MILLAR.

Cyanoethylation of phenylphosphine and of diphenylphosphine occurs readily without use of a catalyst, whereas that of aniline and diphenylamine is vigorously promoted by an acidic catalyst, and that of phenylarsine by a basic catalyst.

The chemical properties of bis-2-cyanoethylphenylphosphine $Ph{\cdot}P(CH_2{\cdot}CH_2{\cdot}CN)_2$ and of 2-cyanoethyldiphenylphosphine $Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}CN$ have been investigated. These compounds, and also 2-carboxyethyldiphenylphosphine, could not be cyclised to keto-phosphines : in this respect they are similar to their arsenic analogues, but differ markedly from their nitrogen analogues.

IT has been shown by R. C. Cookson and Mann (*J.*, 1947, 618; 1949, 67) that combination of aniline and vinyl cyanide, to give *NN*-bis-2-cyanoethylaniline, $Ph{\cdot}N(CH_2{\cdot}CH_2{\cdot}CN)_2$, occurs readily only when the reactants are heated in the presence of acetic acid at 150°, and that the similar conversion of diphenylamine into *N*-2-cyanoethyldiphenylamine, $Ph_2N{\cdot}CH_2{\cdot}CH_2{\cdot}CN$, requires heating in the presence of acetic acid, copper acetate, and metallic copper at 150° (cf. also Braunholtz and Mann, *J.*, 1952, 3046). On the other hand, although the corresponding conversion of phenylarsine and diphenylarsine into bis-2-cyanoethylphenylarsine and 2-cyanoethyldiphenylarsine respectively occurs readily when the reactants are boiled under reflux in the absence of a catalyst, the reaction of the phenylarsine in particular becomes very vigorous in the presence of an alkaline catalyst.

We have therefore investigated the cyanoethylation of the intermediate phenylphosphine and diphenylphosphine. When a mixture of phenylphosphine and an excess of vinyl cyanide was heated at 130—135° for 6 hours, bis-2-cyanoethylphenylphosphine, $Ph{\cdot}P(CH_2{\cdot}CH_2{\cdot}CN)_2$, was formed in 62% yield, calculated on the purified product. Addition of acetic acid to the reaction mixture caused no significant change in yield, but the crude product was now apparently purer, since it could be purified by crystallisation without intermediate distillation. Addition of a trace of sodium methoxide to the reaction mixture, however, decreased the yield to 49%.

Similarly a mixture of diphenylphosphine and vinyl cyanide when heated at 130° for 7 hours gave 2-cyanoethyldiphenylphosphine in 71% yield, which was not appreciably affected by the addition of acetic acid, but the presence of sodium methoxide in the reaction mixture caused the yield to fall to 43%.

These results indicate that the cyanoethylation of primary and secondary phosphines does not require a catalyst, and that the process is thus truly intermediate between the acid-catalysed cyanoethylation of amines and the base-catalysed cyanoethylation of arsines. It also appears probable that the mechanism of the process cannot be the same with the three classes of compound.

We have investigated the properties of the new 2-cyanoethylphosphines. Bis-2-cyanoethylphenylphosphine forms colourless crystals, and has been characterised as the crystalline methiodide and the palladobromide complex $[\{Ph{\cdot}P(CH_2{\cdot}CH_2{\cdot}CN)_2\}_2PdBr_2]$. The phosphine does not form a stable picrate: this is not unexpected, for Braunholtz and Mann (*loc. cit.*) were unable to isolate the picrate of *NN*-bis-2-cyanoethylaniline.

Acid or alkaline hydrolysis of the phosphine furnished bis-2-carboxyethylphenylphosphine, $Ph{\cdot}P(CH_2{\cdot}CH_2{\cdot}CO_2H)_2$, but neither this acid nor its derivatives with potassium palladobromide or palladochloride, or with methyl iodide, could be obtained crystalline. It is noteworthy that Cookson and Mann (*loc. cit.*, 1949) also obtained the corresponding nitrogen derivative as a viscous syrup.

The crystalline 2-cyanoethyldiphenylphosphine has also been characterised as its methiodide and its palladobromide complex: on hydrolysis it readily furnishes the crystalline 2-carboxyethyldiphenylphosphine, $Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, which gives a simple yellow palladobromide complex, $[(C_{15}H_{15}O_2P)_2PdBr_2]$, and an orange-red binuclear complex, $[(C_{15}H_{15}O_2P)_2(PdBr_2)_2]$.

The above cyano- and carboxy-phosphines complete three new eutropic series, the melting points of which are given in the Table.

X	$Ph{\cdot}X(CH_2{\cdot}CH_2{\cdot}CN)_2$	$Ph_2X(CH_2{\cdot}CH_2{\cdot}CN)$	$Ph_2X(CH_2{\cdot}CH_2{\cdot}CO_2H)$
N	81°	41°	112°
P	73	64	126
As	60	38	105

It is noteworthy that *NN*-bis-2-cyanoethylaniline undergoes cyclisation under the influence of aluminium chloride to form 1 : 6-diketojulolidine (Mann and Smith, *J.*, 1951, 1898), and 2-carboxyethyldiphenylamine similarly, when treated with phosphoric anhydride in boiling xylene, gives 1 : 2 : 3 : 4-tetrahydro-4-keto-1-phenylquinoline (Cookson and Mann, *loc. cit.*; Mann, *J.*, 1949, 2816). On the other hand, attempts to carry out similar cyclisations of bis-2-cyanoethylphenylarsine, 2-cyanoethyldiphenylarsine, and 2-carboxyethyldiphenylarsine failed, in spite of a variety of conditions employed (Cookson and Mann, *loc. cit.*). We have now attempted the cyclisation of the phosphorus analogues of these three arsine compounds, but again without success. Of the compounds shown in the above Table, therefore, cyclisation to the corresponding ketones appears to be limited to the nitrogen derivatives.

Since some tertiary phosphines are more strongly basic than the corresponding amines (Davies and Addis, *J.*, 1937, 1622), it is possible that phenylphosphine is also more basic than aniline, although apparently no quantitative data are available. Phenylphosphine, however, when heated with acetic anhydride gives the diacetyl derivative, which we have been unable to obtain crystalline although it is a stable compound in the absence of water, and can be distilled without decomposition. This compound therefore has also been characterised as its crystalline palladobromide complex, of composition $[(Ph{\cdot}PAc_2)_2PdBr_2]$.

EXPERIMENTAL

Phenylphosphine was prepared as described by Mann and Millar (*J.*, 1952, 3039) and stored in sealed weighed ampoules.

Bis-2-cyanoethylphenylphosphine.—(a) *No catalyst.* Phenylphosphine (4·1 g.) and vinyl cyanide (5·9 g., 3 mols.) were added to turn to a glass tube previously cooled in solid carbon dioxide and filled with nitrogen, the tube being then sealed. This technique was employed in order to reduce to a minimum both the foul odour and possible oxidation of the phosphine. The tube was then heated at 130—135° for 6 hours, the mixture forming a pale yellow oil. The cold product, when seeded with the pure tertiary phosphine crystallised, but repeated recrystallisation of this material did not give a pure product. The crude product was therefore distilled, the principal fraction of the phosphine having b. p. 195—205°/0·2 mm., leaving a dark non-volatile residue. The distilled *phosphine* readily crystallised, and when recrystallised from ethanol formed colourless crystals (5 g., 62%), m. p. 72—73° (Found : C, 66·4; H, 5·8; N, 1·29. $C_{12}H_{13}N_2P$ requires C, 66·6; H, 6·05; N, 12·95%).

(b) *Acid catalyst.* Phenylphosphine (2 g.), vinyl cyanide (2·9 g., 3 mols.), and acetic acid (4 c.c.) were treated as above. Excess of solvent was removed by distillation from the syrupy product, and the residue then shaken with saturated aqueous sodium carbonate. The semi-solid product was purified directly by recrystallisation from ethanol : one recrystallisation gave the phosphine, m. p. 68—71° (2·36 g., 60%).

(c) *Basic catalyst.* A mixture of the phosphine (5·5 g.), vinyl cyanide (8 g., 3 mols.), and sodium methoxide (*ca.* 0·005 g.) was heated as in (a). Distillation gave the phosphine (5·25 g., 49%), m. p. 72—73° after recrystallisation from ethanol.

A solution of the phosphine in methyl iodide, when warmed and cooled, deposited the *methiodide,* colourless crystals (from ethanol), m. p. 115° (Found : C, 43·7; H, 4·2; N, 7·75. $C_{13}H_{16}N_2IP$ requires C, 43·6; H, 4·5; N, 7·8%). The methopicrate was not precipitated when ethanolic solutions of this salt and of sodium picrate were mixed.

When an ethanolic solution of a small excess of the phosphine and an aqueous ethanolic potassium palladobromide solution were mixed, boiled, and cooled, lemon-yellow crystals of *dibromodi(bis-2-cyanoethylphenylphosphine)palladium* were deposited, having m. p. 227—228° after recrystallisation from aqueous acetone (Found: C, 41·3; H, 3·4; N, 7·9. $C_{24}H_{26}N_4Br_2P_2Pd$ requires C, 41·2; H, 3·75; N, 8·0%).

Oxidation. An acetone solution of the phosphine was treated at 60° with an excess of hydrogen peroxide, set aside overnight, and then evaporated in a vacuum. The residual crystalline oxide was very soluble in polar solvents and could not be satisfactorily recrystallised.

Hydrolysis. (*a*) The solution of the phosphine in aqueous-ethanolic potassium hydroxide was boiled under reflux in a nitrogen atmosphere. The cold solution was acidified with hydrochloric acid, and the solvent removed under reduced pressure in nitrogen. The residue was extracted with acetone, which on evaporation gave a syrup which could not be induced to crystallise.

(*b*) The phosphine was similarly hydrolysed with concentrated hydrochloric acid; evaporation in a vacuum followed by extraction of the residue with boiling ethanol again afforded a syrup which could not be crystallised.

Diphenylchlorophosphine.—The following modification of Michaelis's method (*Ber.*, 1877, **10**, 627; Michaelis and Link, *Annalen*, 1881, **207**, 208) was found to give the highest yield. A mixture of phenyldichlorophosphine (130 g.) and pure dry diphenylmercury (165 g., 0·64 mol.) was heated in an oil-bath under a slow stream of nitrogen at 200° for 90 minutes with occasional vigorous shaking. Light petroleum (500 c.c.; b. p. 60—80°) was added to the warm reaction mixture, which was boiled for 10 minutes, and the petroleum then decanted. The viscous residue was mixed with half its bulk of dry sand, and the petroleum extraction repeated. Finally the residue was thoroughly kneaded with warm petroleum, transferred to a Buchner funnel, and there sucked as free from petroleum as possible whilst being pressed firmly on to the filter. The solvent from the combined extracts was distilled under nitrogen, and the residue, when fractionated under reduced pressure, gave (*a*) an early fraction of phenyldichlorophosphine (*ca.* 40 c.c.), (*b*) diphenylchlorophosphine, b. p. 178—180°/18 mm. (55 g., 54%). This colourless liquid contained a trace of suspended mercury, which settled out when set aside overnight. Omission of the treatment with sand gave reduced yields (*ca.* 10%), because the reaction product is not readily wetted by petroleum.

Diphenylphosphine.—Malatesta (*Gazzetta*, 1947, **77**, 518) has described the preparation of this phosphine in 40% yield by the action of a considerable excess of phenylmagnesium bromide on tetraphosphorus trisulphide. We have, however, obtained by this method only a low yield of the phosphine contaminated by sulphur derivatives. The following modification of Dörken's method (*Ber.*, 1888, **21**, 1505; cf. also Michaelis and Gleichmann, *Ber.*, 1882, **15**, 801) appears to be the most satisfactory, the reaction involved being formulated by Dörken as :

$$4Ph_2PCl + 3Na_2CO_3 + H_2O = 2Ph_2PH + 2Ph_2PO_2Na + 3CO_2 + 4NaCl$$

Diphenylchlorophosphine (50 g.) was added dropwise during 30 minutes to an agitated solution of anhydrous sodium carbonate (25 g.) in water (80 c.c.) contained in a flask which was fitted with a stirrer, dropping funnel, and reflux condenser, and into which nitrogen was passed throughout the preparation. Carbon dioxide was smoothly evolved and oily drops of the phosphine separated in the solution. The latter was finally warmed to 50° and the mixture stirred for a further 30 minutes. The phosphine was then extracted with benzene, and the extract dried ($CaCl_2$) and fractionally distilled at atmospheric pressure in a stream of nitrogen. The phosphine was obtained as a colourless liquid, b. p. 280—282° (10 g., 47%), and sealed under nitrogen in weighed ampoules.

2-Cyanoethyldiphenylphosphine.—(a) *No catalyst.* A mixture of diphenylphosphine (3·3 g.) and vinyl cyanide (1·9 g., 2 mols.) in a sealed tube, as previously described, was heated at 130° for 7 hours. Distillation of the excess of vinyl cyanide under nitrogen gave a residue which solidified on cooling and when twice recrystallised from methanol gave the *phosphine* as colourless crystals (3 g., 71%), m. p. 64—64·5° (Found : C, 75·5; H, 5·9; N, 5·7. $C_{15}H_{14}NP$ requires C, 75·3; H, 5·9; N, 5·85%). The combined mother-liquors from the recrystallisations were evaporated and the residue was hydrolysed, as described below, to the corresponding acid (0·9 g.), m. p. 124—125°.

(b) *Acid catalyst.* Repetition of the above experiment with the addition of acetic acid (4 c.c.) to the reaction mixture gave the phosphine (2·86 g., 68%), m. p. 63—64°.

(c) *Basic catalyst.* A mixture of diphenylphosphine (6·2 g.), vinyl cyanide (3·5 g., 2 mols.), and sodium methoxide (0·005 g.), when treated as before, gave the required phosphine, which, similarly recrystallised from methanol, also had m. p. 64—64·5° (mixed and unmixed) (3·4 g., 42·5%).

When methyl iodide was added to an ethereal solution of the phosphine, the *methiodide* was slowly deposited as colourless crystals, m. p. 163—164° (Found: C, 50·7; H, 4·5; N, 3·9. $C_{16}H_{17}NIP$ requires C, 50·4; H, 4·5; N, 3·7%). The methopicrate of this salt also could not be prepared in ethanolic solution.

Dibromobis-2-cyanoethyldiphenylphosphine-palladium, prepared as the previous palladium derivative, formed yellowish-brown crystals, m. p. 176°, from ethanol (Found : C, 48·0; H, 4·0; N, 4·1. $C_{30}H_{28}N_2Br_2P_2Pd$ requires C, 48·4; H, 3·8; N, 3·8%).

Hydrolysis. The phosphine (0·48 g.) was added to a solution of potassium hydroxide (0·44 g., 4 mols.) in 50% aqueous ethanol (4·4 c.c.), which was boiled under reflux in a nitrogen atmosphere for 3 hours. The ethanol was then distilled off, and the residual solution diluted with water, cooled, and made just acid to litmus. The precipitated crystalline *2-carboxyethyldiphenylphosphine,* when recrystallised from aqueous ethanol, formed colourless crystals, m. p. 125—127° (Found : C, 69·6; H, 5·6. $C_{15}H_{15}O_2P$ requires C, 69·75; H, 5·9%).

A solution of the acid in aqueous ethanol did not affect Congo-red or evolve carbon dioxide from sodium hydrogen carbonate solution. The acid when dissolved in hot methyl iodide gave an oil which could not be recrystallised.

Dibromobis-2-carboxyethyldiphenylphosphine-palladium was formed when theoretical quantities of the acid and of potassium palladobromide were heated together in boiling ethanol; it formed yellow crystals (from ethanol), m. p. 226—228° (decomp.) (Found : C, 46·2; H, 4·2. $C_{30}H_{30}O_4Br_2P_2Pd$ requires C, 46·0; H, 3·9%).

Dibromobis-2-cyanoethyldiphenylphosphine-μ-dibromopalladium was formed when the acid was similarly treated with an excess of potassium palladobromide, and when recrystallised from methanol formed orange-red crystals, m. p. 239—241° (decomp.) (Found : C, 34·1; H, 3·1. $C_{30}H_{30}O_4Br_4P_2Pd_2$ requires C, 34·3; H, 2·9%).

Attempted Cyclisations.—Since all the attempted cyclisations failed, only a general account of the methods employed is given.

(1) *Bis-2-cyanoethylphenylphosphine.* A solution of this compound in chlorobenzene containing an excess of aluminium chloride was boiled under reflux for 8 hours, but the unchanged phosphine (54%) was subsequently recovered.

(2) *2-Cyanoethyldiphenylphosphine.* (*a*) An experiment similar to (1) ultimately gave the unchanged phosphine (73%). (*b*) The phosphine was added to a fused mixture of aluminium chloride, potassium chloride, and sodium chloride, which was then heated at 175° for 3 hours (cf. F.P. 806,715), but no ketonic product could be isolated.

(3) *2-Carboxyethyldiphenylphosphine.* (*a*) A solution of the acid in xylene, containing phosphoric anhydride and " Hyflo Supercel " in suspension was boiled for 3 hours under reflux in nitrogen. The unchanged acid (14%) was subsequently recovered, in addition to oily products which could not be purified. (*b*) A solution of the acid in benzene was heated first with

phosphorus pentachloride and then with aluminium chloride. Working up gave a small yield of crude 2-benzoylethyldiphenylphosphine oxide, identified as its 2 : 4-*dinitrophenylhydrazone*, yellow-orange crystals (from ethanol), m. p. 234—236° (decomp.) (Found : C, 63·05; H, 4·65; N, 11·4. $C_{27}H_{23}O_5N_4P$ requires C, 63·0; H, 4·5; N, 10·9%). There are many examples of acyl chlorides giving cyclic ketones in benzene solution : in this case, the preferential reaction of the chloride with the solvent confirms the difficulty of the desired cyclisation.

PP-*Diacetylphenylphosphine*.—A mixture of phenylphosphine (2 g.) and acetic anhydride (4 c.c.) in a sealed tube under nitrogen was heated at 130° for 6 hours, giving a colourless liquid free from the odour of unchanged phosphine. The excess of anhydride was removed under reduced pressure, giving a pale amber residual syrup which had a characteristic odour, and could not be crystallised. It distilled without decomposition (b. p. *ca.* 200°/14 mm.), leaving a non-volatile residue, but the distillate did not crystallise. The identity of this (presumably impure) diacetylphenylphosphine was determined by (*a*) its apparent failure to combine with methyl iodide, and (*b*) formation, in hot ethanolic solution, of *dibromobisdiacetylphenylphosphinepalladium*, chocolate brown crystals (from aqueous ethanol), m. p. 183—185° (preliminary decomp.) (Found : C, 37·5; H, 3·65. $C_{20}H_{22}O_4Br_2P_2Pd$ requires C, 37·0; H, 3·4%).

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