Co-ordination Compounds of Boron Trifluoride and Organic Esters.

By GILBERT T. MORGAN and RAYMOND TAYLOR.

WE had found that the action of boron trifluoride on methyl and ethyl esters of formic and acetic acids resulted in the formation of crystalline products $R{\cdot}CO_2X,BF_3$ (where $R = H$ or CH_3 and $X = CH_3$ or C_2H_5) and had supplied Dr. Sugden with this series of compounds for researches on the parachor of boron (Sugden and Waloff, *v. supra*) when the appearance of a paper by Bowlus and Nieuwland (*J. Amer. Chem. Soc.*, 1931, **53**, 3835) rendered superfluous any detailed account of our experiments. To the note which has already appeared (*Chem. and Ind.*, 1931, **50**, 869) we now wish to make the following additions.

Methyl benzoate boron trifluoride, $C_6H_5{\cdot}CO_2Me,BF_3$, separated from a mixture of its generators, on cooling, in colourless tabular crystals, m. p. 40—55° (decomp.) (Found: C, 46·2; H, 4·1; B, 5·3. $C_8H_8O_2,BF_3$ requires C, 47·1; H, 3·95; B, 5·3%).

Boron trifluoride and methyl salicylate interacted with evolution of hydrogen fluoride. The pale yellow, crystalline product, after being washed successively with methyl salicylate and petroleum (b. p. 40—60°), sublimed under 20 mm. pressure to yield colourless feathery crystals, m. p. 128°. The analytical numbers approximated to $C_8H_8O_3,BF_2$, which suggested partial replacement of fluorine by hydroxylic oxygen and co-ordination of the residual BF_2 with the ester group, so that the compound had a composition analogous to that of the condensation products of boron trifluoride and the β-diketones (Morgan and Tunstall, J., 1924, **125**, 1963).

Boron trifluoride and methyl glycollate interacted with but slight evolution of hydrogen fluoride, and the product when distilled at 62—66°/4 mm. gave a colourless liquid, b. p. 60°/3 mm., approximating in composition to a simple additive compound $C_3H_6O_3,BF_3$.

CHEMICAL RESEARCH LABORATORY,
TEDDINGTON, MIDDLESEX.

[*Received, April 5th*, 1932.]

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201. *Pyridine Arsenicals.*

By NIAL PATRICK MCCLELAND and ROBERT HUGH WILSON.

THE preparation of several compounds in which arsenic is attached to a carbon atom of a pyridine nucleus has been recorded by Tschitschibabin and Kirsanow (*Ber.*, 1927, **60**, 766) and Binz and Räth and their collaborators (*Annalen*, 1927, **455**, 127; 1930, **484**, 52). As yet, however, no secondary or tertiary pyridine arsenicals have been reported.

Binz, Räth, and Gante (*Annalen*, 1928, **467**, 11) have reported the preparation of pyridyl-3-arsonic acid by eliminating the chlorine from 2-chloropyridyl-5-arsonic acid, but do not seem to have obtained it pure. (They say that it is " Eine farblose, undeutlich krystalline Masse," m. p. 112—113°, hygroscopic, and not soluble in alcohol, and make no mention of recrystallisation.)

As this method did not provide a ready means of preparing the simpler pyridine arsenicals, we investigated the action of arsenious chloride on 3-chloromercuripyridine (McCleland and Wilson, this vol., p. 1263), and thus obtained the *hydrochloride* of 3-pyridyldichloroarsine, and from this *pyridyl*-3-*arsonic acid*, the properties of which differed considerably from those reported by Binz, Räth, and Gante, as it was isolated as white prisms, m. p. 158—159°, not deliquescent, and soluble in alcohol (18 g. in 100 c.c.). We failed to obtain the 3-pyridyldichloroarsine which these authors claim to have obtained by reducing their acid with sulphur dioxide in hydrochloric acid solution, and came to the conclusion that it could not exist in the presence of moisture, as it would hydrolyse to a mixture of the hydrochloride and pyridyl-3-arsenoxide.

Di-3-pyridylchloroarsine was made by heating together 3-pyridyldichloroarsine hydrochloride and pyridyl-3-arsenoxide, and isolated as the *dihydrochloride*. *Tri*-3-*pyridylarsine oxide* was prepared by distilling pyridyl-3-arsenoxide under reduced pressure, and oxidising the product with hydrogen peroxide. These reactions are precisely analogous to those of the corresponding phenyl compounds.

Räth (*Annalen*, 1931, **486**, 95) has shown that 3-aminopyridine gives most of the reactions of aniline, but mentions the Bart reaction, the Schmidt reaction for antimony compounds, and the Leuckhardt thiophenol synthesis as important exceptions. Binz, Räth, and Gante (*loc. cit.*) have suggested that its failure to show these reactions is due to the basicity of the pyridine nucleus, since substituted 3-aminopyridines in which the basicity is weakened by negative substituents in the 2- or 6-position react readily. Having established the properties of pyridine arsenicals, and especially that 3 : 3′-arsenopyridine is readily soluble in hydrochloric acid, but not in ammonium hydroxide, we attempted the Bart reaction under standard conditions, and obtained a yield of 6% of pyridyl-3-arsonic acid, identical with that obtained from 3-chloromercuripyridine.

EXPERIMENTAL.

3-*Pyridylchloroarsine Hydrochloride.*—Crude 3-chloromercuripyridine (35 g.) was boiled for 5 hours with arsenious chloride

(50 c.c.). The excess of arsenious chloride was distilled off under reduced pressure, and the residue extracted with alcohol. The extract was treated with animal charcoal in the cold, and evaporated to small bulk. The *hydrochloride* crystallised on addition of concentrated hydrochloric acid. When hydrogen chloride was passed into an aqueous solution of the crude product, it separated in white prisms, with one molecule of water of crystallisation, which was lost on heating at 100° for 2 hours; m. p., with loss of hydrogen chloride, 216—233°; yield, 8·5 g. (Found: Cl, 38·3; loss, 2 hrs./100°, 6·5. $C_5H_5NCl_3As,H_2O$ requires Cl, 38·2; H_2O, 6·5%. Found, after 2 hours' heating at 100°: C, 23·3; H, 2·2; Cl, 40·9. $C_5H_5NCl_3As$ requires C, 23·1; H, 2·2; Cl, 40·8%).

In an attempt to make the 3-pyridyldichloroarsine described by Binz, Räth, and Gante, 4·2 g. of the hydrochloride were treated with 16·1 c.c. (1 mol.) of *N*-sodium hydroxide solution, and the product was evaporated to dryness. The solid residue was extracted with alcohol. Crystals of the original compound separated from the extract, together with a gum. The whole was distilled (210—250°/10 mm.). The gummy distillate set to a hard glass on cooling, which gave with water chiefly 3 : 3′-dipyridylchloroarsine dihydrochloride (1·7 g.), m. p. and mixed m. p. 283—285°.

Pyridyl-3-arsonic Acid.—(1) 3-Pyridyldichloroarsine hydrochloride (10 g.) was dissolved in water (100 c.c.), and sodium hypophosphite (20 g.) and concentrated hydrochloric acid (20 c.c.) added. The solution when warmed on a water-bath became yellow, but no precipitate separated until it was made alkaline with ammonia. The flocculent yellow-green precipitate then formed (4·5 g., presumed to be 3 : 3′-arsenopyridine) was oxidised with "20-volume" hydrogen peroxide in the presence of ice, the solution obtained evaporated to dryness in a vacuum desiccator, the product extracted with alcohol, and the extract evaporated to dryness. The residue slowly crystallised, and on recrystallisation from alcohol 2·7 g. of white prisms, m. p. 158—159°, were obtained (Found: C, 29·7; H, 3·1. $C_5H_6O_3NAs$ requires C, 29·6; H, 3·0%).

The *hydrochloride* of this *acid* was prepared by dissolving 0·5 g. in hydrochloric acid, evaporating the solution to dryness, and crystallising the solid residue from alcohol; m. p. 196—198° (Found: Cl, 14·8. $C_5H_6O_3NAs,HCl$ requires Cl, 14·8%).

(2) 3-Aminopyridine (5 g.) was diazotised, and the solution added to a solution of arsenious oxide (11·5 g.) and sodium carbonate (16·5 g.) in water (200 c.c.) at 40°, 2 c.c. of saturated copper sulphate solution being added as a catalyst. The solution was treated with animal charcoal, acidified with hydrochloric acid, and warmed on a water-bath with sodium hypophosphite (20 g.) for 3 hours. The

dark brown precipitate was filtered off, and the filtrate made alkaline with ammonia. The flocculent precipitate was oxidised as above, and the acid isolated by crystallising its hydrochloride from alcohol. Yield, 0·7 g.; m. p. and mixed m. p. of the hydrochloride, 195—197°; m. p. and mixed m. p. of the acid, 158—159° (Found: N, 6·9. $C_5H_6O_3NAs$ requires N, 6·9%).

Di-3-pyridylchloroarsine Dihydrochloride.—3-Pyridyldichloroarsine hydrochloride (10 g.) was titrated with sodium hydroxide until neutral to litmus. The solution was evaporated to dryness, the residue extracted with alcohol, the extract evaporated, and the product heated with 2 g. of the hydrochloride for 2 hours at 200°. The melt was extracted with alcohol, and the extract evaporated with hydrochloric acid; the residue crystallised from water in white prisms (6·8 g.), m. p. 283—285° (Found: C, 35·5; H, 3·0; Cl, 31·3, 31·2. $C_{10}H_8N_2ClAs,2HCl$ requires C, 35·3; H, 2·9; Cl, 31·4%).

In an attempt to prepare di-3-pyridylchloroarsine, 3 g. of the dihydrochloride were treated with 17·7 c.c. (2 mols.) of *N*-sodium hydroxide. The product was evaporated to dryness, extracted with alcohol, and distilled at 207—210°/10 mm. The distillate crystallised on cooling, but no definite m. p. could be obtained (Found: Cl, 13·0. $C_{10}H_8N_2ClAs$ requires Cl, 13·3%).

Di-3-pyridylarsonic Acid.—Di-3-pyridylchloroarsine dihydrochloride (1·5 g.) was titrated with sodium hydroxide solution (litmus) and treated as described above. The gum remaining after evaporation of the alcohol was titrated with hydrogen peroxide until the solution turned starch–iodide paper blue, and evaporated on a water-bath. The *acid* crystallised from water in white prisms, m. p. 203—204° (Found: C, 45·4; H, 3·4. $C_{10}H_9O_2N_2As$ requires C, 45·4; H, 3·4%).

Tri-3-pyridylarsine Oxide.—3-Pyridylchloroarsine hydrochloride (9·5 g.) was titrated with sodium hydroxide and treated as described above. The residue from the alcoholic extract was distilled (metal bath at 320—360°/10 mm.). The gum extracted from the distillate with alcohol was oxidised by titration with hydrogen peroxide until the solution turned starch–iodide paper blue. The residue after evaporation of the solution to dryness crystallised from alcohol, but could not thus be purified. It was converted into the *trihydrochloride*, which crystallised from alcohol in white needles (2·4 g.), m. p., with loss of hydrogen chloride, 221° (Found: Cl, 24·2, 24·4. $C_{15}H_{12}ON_3As,3HCl$ requires Cl, 24·5%). The *oxide* recovered from the hydrochloride crystallised from absolute alcohol in white needles, m. p. 226° (Found: C, 55·6; H, 4·0; N, 12·9. $C_{15}H_{12}ON_3As$ requires C, 55·4; H, 3·7; N, 12·9%).

THE UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

[*Received, March 18th,* 1932.]