Summary

Addition compounds containing three molecules of phenylboric acid and one of an amine with the elimination of two molecules of water have been described. Bases as strong as pyridine, but not nitriles, aniline or diphenylamine, form stable addition compounds. The structure of these compounds and a mechanism for their formation have been presented.

BERKELEY, CALIFORNIA RECEIVED OCTOBER 19, 1932
PUBLISHED APRIL 6, 1933

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON UNIVERSITY]

The Preparation of 4-Fluoro- and 4,4′-Difluorobenzophenone

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In connection with an investigation in progress in this Laboratory it was desired to obtain some 4-fluoro- and 4,4′-difluorobenzophenone. The first of these has been previously prepared by Koopal through the condensation of *p*-fluorobenzoyl chloride with benzene,[1] but the second does not appear to have been prepared. Since it has been shown that when phthalic anhydride is condensed with fluorobenzene by means of aluminum chloride the condensation takes place exclusively in the para position with respect to the fluorine atom,[2] it would be expected that the condensation with benzoyl chloride would take place in a similar manner.

As the first step in this investigation, it was shown that 4-fluorobenzophenone can be obtained through the condensation of benzoyl chloride with fluorobenzene, the product so prepared being identical with that resulting from Koopal's procedure, with no more than traces of the isomeric 2-fluorobenzophenone being formed. Similarly, the condensation of *p*-fluorobenzoyl chloride with fluorobenzene gave almost exclusively 4,4′-difluorobenzophenone. The product in this case was identified by subjecting its oxime to a Beckmann rearrangement, followed by hydrolysis to *p*-fluoroaniline and *p*-fluorobenzoic acid.

Experimental Part

4-Fluorobenzophenone.—A condensation of 18 g. of benzoyl chloride and 25 g. of fluorobenzene, using 20 g. of anhydrous aluminum chloride, working up the product in the usual way, gave 17 g. (66%) of colorless crystals, m. p. 48.2–48.7° from petroleum ether. A mixed melting point, using an authentic preparation made according to Koopal's method, m. p. 48.4–48.9 (Koopal gives 52°), demonstrated that both products were identical.

Anal. Calcd. for $C_{13}H_9OF$: F, 9.50. Found: F, 9.70, 9.64.

Evaporation of the mother liquors from the first two crystallizations gave less

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[1] Koopal, *Rec. trav. chim.*, **34**, 157 (1915); *Chem. Zentr.*, II, 332 (1915).

[2] Hahn and Reid, THIS JOURNAL, **46**, 1645 (1924).

than 1 g. of a mixture of crystals and an oil which was not identified, showing that at most only a minute amount of 2-fluorobenzophenone had been formed.

4,4′-Difluorobenzophenone.—A similar procedure starting with 25.4 g. of *p*-fluorobenzoyl chloride, 35 g. of fluorobenzene and 30 g. of anhydrous aluminum chloride yielded 18.5 g. (52%) of colorless crystals, m. p. 107.5–108.5° from petroleum ether.

Anal. Calcd. for $C_{13}H_8OF_2$: F, 17.42. Found: F, 17.46, 17.35.

Evaporation of the mother liquor from the first crystallization gave about 1 g. of material melting at approximately 100°, indicating that only a very small amount at most of 4,2′-difluorobenzophenone had been formed.

4,4′-Difluorobenzophenoneoxime.—To a mixture of 5 g. of 4,4′-difluorobenzophenone, 3 g. of hydroxylamine hydrochloride, 6 cc. of water and 15 cc. of alcohol there was added in small quantities with shaking 5.5 g. of powdered sodium hydroxide. The mixture was boiled for five minutes and was then poured into a solution of 15 cc. of concd. hydrochloric acid in 100 cc. of water. The solid product was filtered off, dried and crystallized twice from toluene; m. p. 137–138°.

Rearrangement of 4,4′-Difluorobenzophenoneoxime.—To a solution of 2 g. of the oxime in 50 cc. of anhydrous ether there was added 5 g. of powdered phosphorus pentachloride. The ether was distilled off on the steam-bath and the residue was treated with 25 cc. of water. The product was filtered off, dried and recrystallized from alcohol, m. p. 183.5–184.2°.

Hydrolysis of *p*-Fluorobenzo-*p*-fluoroanilide.—One and one-half grams of the anilide was boiled with 200 cc. of constant boiling hydrochloric acid for six hours. An excess of 10% sodium hydroxide was added to the solution and it was distilled until the distillate no longer gave a precipitate with bromine water. About 0.5 g. of a light brown, oily liquid was extracted from the distillate with ether. On treatment with acetyl chloride, this gave a product melting at 150.8–151.3° after crystallization from water, in agreement with the value given by Holleman for the melting point of *p*-fluoroacetanilide.[3]

On acidifying the residue from the distillation with hydrochloric acid, there was obtained *p*-fluorobenzoic acid.

Summary

1. It has been shown that the condensation of benzoyl chloride and of *p*-fluorobenzoyl chloride with fluorobenzene takes place almost exclusively in the para position with respect to the fluorine atom.

2. 4,4′-Difluorobenzophenone has been prepared.

St. Louis, Missouri

Received October 20, 1932
Published April 6, 1933

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(3) Holleman, *Rec. trav. chim.*, **25**, 330 (1906); *Chem. Zentr.*, II, 1830 (1906).