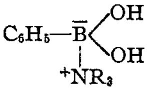
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

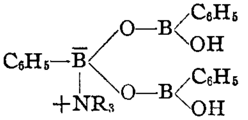
# Addition Compounds of Phenylboric Acid with Bases

BY DAVID L. YABROFF AND G. E. K. BRANCH

An addition compound of diethylamine and phenylboric acid was described in a brief communication.[1] There it was found that this compound contained three molecules of phenylboric acid to one of the amine. It was thought at first that loss of a molecule of water had occurred with the hydrogen of the amine and an hydroxyl group of the phenylboric acid, this being followed by addition of more phenylboric acid to the compound. It was pointed out that the analyses then obtained did not preclude the possibility of loss of a water molecule from the product. Since then we have investigated the action of other bases on phenylboric acid. The results obtained may be briefly summarized. (1) Addition compounds containing one mole of the amine and three moles of phenylboric acid are always obtained regardless of the nature (primary, secondary or tertiary) of the amine. (2) Bases as strong as pyridine will form stable compounds whereas weaker bases including aniline, nitriles, diphenylamine and acetic anhydride do not form stable addition products. (3) The percentage of carbon obtained for the diethyl and triethylamine compounds seems to indicate that two molecules of water have been eliminated from the product. Analyses of the propylamine compound are not self-consistent and seem to indicate the presence of an indefinite amount of water.

In view of results (1) and (3), the following mechanism appears probable


"A"


"B"

A molecule of the amine combines with one of phenylboric acid yielding "A." The base strength of the hydroxyl oxygens is increased by the proximity of the negative charge on the boron atom, and combination with two more molecules of phenylboric acid occurs on the oxygen atoms. This is now stabilized by loss of two molecules of water, giving the stable product "B," which is actually isolated.

## Experimental Section

**Materials.**—Phenylboric acid was prepared according to the method of Krause and Nitsche[2] by passing boron trifluoride into an ethereal solution of phenylmagnesium bromide. The boron trifluoride was prepared according to the method of Ruff[3] by heating a mixture of sulfuric acid, cryolite and boric oxide. The gas was passed through two freezing traps and through a tower containing a mixture of potassium fluoride and

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[1] Branch and Yabroff, THIS JOURNAL, **54**, 2569 (1932).

[2] Krause and Nitsche, *Ber.*, **55**, 1261 (1922).

[3] Ruff, "Die Chemie des Fluors," 1920, p. 25.

fused boric oxide before entering the Grignard solution. The amines were dried over solid potassium hydroxide and fractionally distilled.

**Analyses.**—Combustions were carried out in a tube containing two parts of copper oxide and one part of lead chromate in an atmosphere of air. A reduced copper spiral was placed at the end of the tube to reduce oxides of nitrogen. After most of the sample had been burned the tube was heated to redness in a stream of oxygen. The percentage carbon was always low, which was probably due to occlusion of charred particles by the boric oxide formed. The former method[1] used for the determination of nitrogen was found to give low results. Kjeldahl analyses which had been digested for twelve to twenty hours with 10 g. of potassium sulfate and 3 grams of potassium persulfate were found to give fairly good results even for the pyridine and piperidine compounds. Boron analyses were obtained by decomposing the compound by refluxing in alkaline solution, neutralizing to the methyl red end-point, and titrating with sodium hydroxide solution in the presence of glycerine with phenolphthalein as the indicator.

**Procedure.**—The amine (1 mole) and phenylboric acid (3 moles) were dissolved in dry ether. It was found that small amounts of water had no apparent effect on the reaction so no special precautions were taken to exclude moisture. Occasionally the addition product precipitated at once. Usually, however, part of the ether was evaporated and the mixture cooled in order to obtain precipitation. In certain cases petroleum ether was added and the solution evaporated to a very small volume. It was very difficult in certain cases to reproduce results once obtained. We varied the concentrations of the substances, tried the effect of small amounts of water and tried different temperatures, but were unable to determine the factors upon which the ease of precipitation of the compounds depended. The solid compounds obtained were washed with dry petroleum ether and evacuated for three hours. They were all stable in air. The propylamine compound did not precipitate so the ether was evaporated off and the residue recrystallized from hot kerosene, yielding a tan solid. Succeeding attempts always yielded an immediate white precipitate which varied in composition and melting point, so it was not investigated further. The compounds prepared and the analyses obtained are given in Table I.

TABLE I

| | Amine | Color | M. p., °C. | Formula |
|---|---|---|---|---|
| 1 | Diethylamine | White | 85 | $(C_6H_5B(OH)_2)_3 \cdot (C_2H_5)_2NH \cdot 2H_2O$ |
| 2 | Triethylamine | White | 39 | $(C_6H_5B(OH)_2)_3 \cdot (C_2H_5)_3N \cdot 2H_2O$ |
| 3 | Propylamine | Tan | 140–143 | $(C_6H_5B(OH)_2)_3 \cdot C_3H_7NH_2 \cdot 2H_2O$ |
| 4 | Pyridine | White | 148–149 | $(C_6H_5B(OH)_2)_3 \cdot C_5H_5N \cdot 2H_2O$ |
| 5 | Piperidine | Pink | 213 | $(C_6H_5B(OH)_2)_3 \cdot C_5H_{11}N \cdot 2H_2O$ |

Percentage composition

| | Carbon | | Hydrogen | | Nitrogen | | Boron | |
|---|---|---|---|---|---|---|---|---|
| | Calcd. | Found | Calcd. | Found | Calcd. | Found | Calcd. | Found |
| 1 | 65.5 | 65.0 65.2 | 7.0 | 7.2 7.2 | 3.5 | 3.3 3.2 | 8.1 | 7.7 7.9 |
| 2 | 66.8 | 66.2 66.2 | 7.5 | 7.7 7.3 | 3.3 | 3.2 3.2 | 7.5 | 7.5 7.6 7.5 |
| 3 | 64.8 | 61.4 59.8 | 6.8 | 6.7 6.6 | 3.6 | 3.7 3.7 | | |
| 4 | | | | | 3.4 | 3.2 3.3 | 7.9 | 7.8 8.0 |
| 5 | | | | | 3.4 | 3.2 2.8 | 7.8 | 7.8 7.5 |

Acetonitrile, benzonitrile, phenylacetonitrile, aniline, diphenylamine, acetic anhydride, acetylacetone and the sodium salt of acetylacetone failed to form stable addition compounds with phenylboric acid.

In conclusion we wish to express our thanks to Mr. A. C. Paiva, who kindly carried out the combustions.

## 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.

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

BY R. D. DUNLOP WITH JOHN H. GARDNER

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).