

Growth-promoting Action.—Initial tests by Dr. C. F. Moreland on tomato leaves showed furfuryl formate to be ineffective in giving an epinastic response. On this tentative basis, it appears probable that the formate does not possess the growth-promoting power which Traub⁸ reported as a conspicuous characteristic of furfuryl acetate and a number of other furan derivatives.

Attempted Preparation of Furfuryl Oxalate.—(1) Oxalic acid and furfuryl alcohol were mixed, ether was added, and the mixture was refluxed with stirring for eight hours; there was no reaction. (2) Furfuryl acetate (0.75 mole) and oxalic acid (0.67 mole) were heated together at 70°, with stirring, for five hours; there was no apparent reac-

tion. The temperature was then raised. At about 85–90° there was an explosion which scattered a black tarry material over a circle of ten feet radius.

Summary

Furfuryl formate has been prepared in fair yield by the reaction between furfuryl alcohol and acetyl formate at 60°. Its properties have been ascertained and some of its reactions have received preliminary study. Attempts to prepare furfuryl oxalate were unsuccessful.

BATON ROUGE, LOUISIANA

RECEIVED MARCH 16, 1942

(8) Traub, *Proc. Am. Soc. Hort. Sci.*, **35**, 438 (1937).

[CONTRIBUTION NO. 71 FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF UTAH]

Organoboron-Nitrogen Compounds. II. The Reaction of Boron Chloride with *p*-Toluidine

BY CORLISS R. KINNEY AND MARTIN J. KOLBEZEN

In an earlier paper the results of a study of the salt of aniline and boron chloride ($C_6H_5NH_2BCl_3$) were described¹ which indicated that several types of organoboron-nitrogen compounds could be made from such salts or addition compounds by the elimination of the halogen acid. In order to determine the extensiveness of these reactions the behavior of *p*-toluidine and boron chloride was studied and is described in the experimental part.

Experimental Part

The Salt of *p*-Toluidine and Boron Chloride, $CH_3C_6H_4NH_2BCl_3$.—A 500-ml. two-necked flask equipped with a mercury-sealed stirrer and a dropping funnel was used. Into the flask, 114 g. of sodium dried benzene was introduced and 13.9 g. (0.118 mole) of boron chloride was distilled into the benzene. The flask was cooled with snow and 9.7 g. (0.0906 mole) of *p*-toluidine dissolved in 127 g. of dry benzene was dropped in slowly and with stirring. With the dilute solutions used the precipitate redissolved immediately but, toward the end, 180 g. more benzene was added and the cooling bath removed in order that the product be kept in solution. When more concentrated solutions were used, the addition compound separated as a white powder which could not be purified readily.

When all of the *p*-toluidine had been added, the stirrer and dropping funnel were removed and the clear solution vacuum distilled. The pressure was about 370 mm. A fine stream of dry carbon dioxide was admitted to minimize bumping. When about one-half of the benzene had been removed, the distillation was stopped and the crystals which had formed filtered out. The filtrate was concentrated to about 50 ml. and a second crop of crystals ob-

tained. The product weighed 19.4 g., a yield of 95.4%. Considering the material left in the 50 ml. of mother liquor, the reaction must proceed quantitatively.

The product was decomposed rapidly by the moisture in the air. Filtrations were made using a Büchner funnel into which was fitted a rubber stopper carrying a tube connected with a source of dry air. The melting point was 159–160° with evolution of hydrogen chloride. Also, when dissolved in dry boiling benzene, hydrogen chloride was evolved and the product obtained on cooling had a melting point of 147–149°. The salt is quite insoluble in cold benzene or other anhydrous solvent and further attempts at recrystallization were unsuccessful. The solubility was determined to be 0.896 g. per 100 ml. of dry benzene at 27°.

*Anal.*¹ Calcd. for $CH_3C_6H_4NH_2BCl_3$: B, 4.83; Cl, 47.48. Found: B, 4.87, 4.81, 4.83; Cl, 47.32, 47.32, 47.14.

On heating the salt to its melting point or in boiling benzene, hydrogen chloride was evolved with no evidence of boron chloride. The number of equivalents of hydrogen chloride was determined by heating 0.0059 mole with boiling benzene. A current of dry carbon dioxide was used to remove the hydrogen chloride which on titration required 0.0124 equivalent of base. The chloride ion was determined gravimetrically and 0.0120 mole was found, which demonstrated that the acid was entirely hydrogen chloride within a small error because, if boron trichloride had been liberated, three equivalents of hydrogen chloride and one of boric acid would have been produced. Similar quantitative results were obtained when the salt was heated dry.

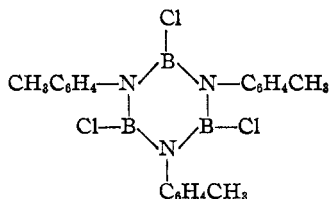
Tri-*p*-tolyltrichlorotriboron-nitride ($CH_3C_6H_4NBCl_3$).—The clear colorless benzene solution obtained by refluxing the addition compound until no more hydrogen chloride was evolved was concentrated and allowed to cool. From the solution a colorless compound slowly crystallized,

(1) Jones and Kinney, *This Journal*, **61**, 1378 (1939).

usually taking two or three days for complete crystallization. The crystals were proved to contain benzene of crystallization by removing the benzene and making the dinitro derivative. On standing in air the crystals became opaque and eventually fell to a powder. The melting point was 308–309° with slight softening at 304°. The substance darkened on melting and if heated for some time turned black, indicating extensive decomposition.

Anal. Calcd. for $(\text{CH}_3\text{C}_6\text{H}_4\text{NBCl})_3 \cdot \text{C}_6\text{H}_6$: B, 6.10; Cl, 20.00; C_6H_6 , 14.66; mol. wt., 532. Found: B, 6.15, 6.02, 6.10; Cl, 20.09, 19.81, 20.07; C_6H_6 , 15.55; mol. wt. in freezing benzene, 505–492, 526–556, 512–524.

This is clearly the benzene addition product of the trimer which may be assigned the cyclic structure



The compound decomposes slowly in air giving off hydrogen chloride fumes, but appears to be quite stable when kept under dry benzene. It is quite insoluble in cold anhydrous solvents such as benzene, carbon tetrachloride, ethyl acetate or ether. It reacts slowly with cold water and rapidly with hot forming *p*-toluidine hydrochloride and presumably boric acid. With 95% alcohol or moist ether the compound dissolves rapidly and heat is liberated. In an attempt to hydrolyze the compound to a trihydroxy derivative corresponding to that obtained with the phenyl homolog,¹ a dry benzene solution was mixed with moist benzene. However, only *p*-toluidine hydrochloride and boric acid could be isolated.

Boric Tri-*p*-toluidide $(\text{CH}_3\text{C}_6\text{H}_4\text{NH})_3\text{B}$.—To 8.9 g. of boron chloride dissolved in 85 g. of dry benzene and cooled in a freezing mixture, 41.7 g. of *p*-toluidine dissolved in 83 g. of benzene was added slowly while the mixture was stirred constantly. The amount of toluidine was 2.5 g. less than the calculated to account for the loss of boron chloride in the early stages of the reaction. When the addition was complete, the cooling bath was replaced by an oil-bath and the reaction mixture refluxed with constant stirring for three hours. The temperature of the oil-bath was 110°.

The mixture was filtered hot using suction. The precipitate of toluidine hydrochloride was returned to the reaction flask and extracted with 200 ml. of boiling benzene for ten minutes. The benzene was filtered and combined with the first filtrate. The residue gave no test for boron,

but did give tests for nitrogen and chlorine. The melting point was 240.5° and was not lowered by admixture with *p*-toluidine hydrochloride (m. p. 241°).

The combined filtrates were distilled to a volume of 40 ml. On cooling fine colorless needles formed which were filtered, washed with dry benzene, and dried in a current of dry air; the yield was 35%. More of the product was obtained from the mother liquor, but this was impure and was not easily purified.

The substance was recrystallized readily from dry benzene, crystallization occurring suddenly. The melting point was 165–166°. On cooling and remelting, the melting point was not lowered, indicating that no decomposition had occurred.

Anal. Calcd. for $(\text{CH}_3\text{C}_6\text{H}_4\text{NH})_3\text{B}$: B, 3.29. Found: B, 3.28, 3.29.

The compound was hydrolyzed easily and was not stable in air. Even in a desiccator over calcium chloride, the odor of toluidine soon became apparent. However, the compound could be kept apparently indefinitely when covered with dry benzene.

The compound reacted readily with dry hydrogen chloride in a benzene solution, forming a solid product. No boron chloride or other boron compound was carried out in sufficient quantities to give the characteristic green flame of boron when ignited. The solid product, in part, reacted violently with water and part dissolved more slowly. No method was found for purifying the product. However, when it was heated with boiling benzene, hydrogen chloride was evolved, the boron containing material passed into solution, and the solid remaining was identified as *p*-toluidine hydrochloride melting at 241°. From the benzene extract, the trimer, tri-*p*-tolyltrichlorotriboron-nitride, was obtained. All of these observations indicate that the product was a mixture of the addition compound, $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2\text{BCl}_3$, and *p*-toluidine hydrochloride.

Summary

The reactions of *p*-toluidine with boron trichloride have been investigated. The addition salt $\text{CH}_3\text{C}_6\text{H}_4\text{NH}_2\text{BCl}_3$ was prepared. Upon heating it evolved hydrogen chloride and formed a trimer which was named tri-*p*-tolyltrichlorotriboron-nitride and was assigned a cyclic structure. By heating the salt with an excess of *p*-toluidine, boric tri-*p*-toluidide $(\text{CH}_3\text{C}_6\text{H}_4\text{NH})_3\text{B}$ was obtained. By treating boric tri-*p*-toluidide with excess dry hydrogen chloride the reaction was reversed.

SALT LAKE CITY, UTAH RECEIVED FEBRUARY 24, 1942