

[CONTRIBUTION FROM THE CHARLES EDWARD COATES LABORATORY OF CHEMISTRY AT LOUISIANA STATE UNIVERSITY]

## Furfuryl Formate

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Furfuryl formate does not appear to have been prepared previously. Tobie<sup>2</sup> attempted this by mixing furfuryl alcohol with formic acid, whereupon the mixture became hot and a violent explosion resulted. The present authors succeeded in preparing it by employing the reaction of furfuryl alcohol with acetyl formate<sup>3</sup> at a moderate temperature: after unsuccessful attempts (1) by treatment of furfuryl alcohol with formic acid at temperatures from 0 to 25°, (2) by refluxing these materials in low-boiling organic solvents, (3) by treatment of furfuryl chloride with sodium formate, (4) by alcoholysis, using *n*-heptyl formate and furfuryl alcohol, distilling slowly at atmospheric pressure, and (5) by treatment of furfuryl alcohol with formamide at 100 to 120°.

**Preparation of Acetyl Formate.**—Following Béhal,<sup>4</sup> three moles of formic acid and four moles of acetic anhydride were mixed and heated at 50° for one hour. Because of the difficulty of protecting a vacuum pump from the quantity of corrosive fumes evolved, Béhal's method of separation of the product was modified conveniently by employing an aspirator, distilling at 45 mm., and collecting distillates at 43–46° and 42–43.5°, respectively, before and after washing with petroleum ether.

**Furfuryl Formate.**—To a mixture of 2.5 moles of furfuryl alcohol<sup>5</sup> and 0.75 mole of sodium formate in a flask with a mercury-seal stirrer, 3.4 moles of acetyl formate was added dropwise. The flask was cooled with tap water during the addition, and then immersed in a water-bath at 60° for five hours. Stirring was continuous during addition and subsequent heating. The resultant mixture was separated by addition of water, in which the ester was nearly insoluble. The ester layer was withdrawn, shaken with saturated aqueous sodium bicarbonate, separated again, and dried over anhydrous sodium sulfate. It was then distilled four times at 16 mm., using a 45-cm. Widmer column; yield 138 g. (44%) of an almost constant-boiling product.

With another batch, a second water washing was employed after the first distillation; only one additional distillation was then required. The product appeared to be equal in quality to the first batch, but the yield was lower.

*Anal.* Calcd. for C<sub>6</sub>H<sub>6</sub>O<sub>3</sub>: C, 57.12; H, 4.80; mol. wt., 126.0. Found: C, 57.41; H, 5.07; mol. wt. (Cottrell), 127.4.

(1) From a thesis submitted by Leslie H. Reeves in partial fulfillment of the requirements for the degree of Master of Science.

(2) Tobie, *Ind. Eng. Chem., News Ed.*, **19**, 72 (1940).

(3) The mixed anhydride of formic and acetic acids.

(4) Béhal, *Compt. rend.*, **128**, 1460 (1899).

(5) The authors wish to thank Dr. F. N. Peters and the Quaker Oats Company for a gift of the furfuryl alcohol used in these experiments.

Saponification of the ester with aqueous sodium hydroxide yielded furfuryl alcohol (identified by the melting point of its  $\alpha$ -naphthyl urethan) and the salt of formic acid (identified by Duclaux constant determinations).

The high carbon content, and the fact that the boiling point was higher than might have been predicted from a study of the data on other furfuryl esters, suggest some contamination of the product by furfuryl alcohol, a difficult substance to eliminate completely. It may be observed, however, that Zanetti<sup>6</sup> has suggested that the accepted boiling point of furfuryl acetate may be several degrees too low. If this is true, the boiling point of the formate occupies a more nearly regular position in the series.

Furfuryl formate is a colorless liquid with a pleasant odor; b. p. 66.2–66.5° (16 mm.), 166.3° (with some coloration) (760 mm.);  $d_{25}^{25}$  1.1584;  $d_{4}^{0}$  1.1830;  $n_{25}^{25}$  1.4662. The sample obtained as described did not crystallize at –68°. Sealed in a glass tube, it turned faintly yellow on standing two months; exposed to air, it darkened rapidly. One hundred grams of water at 25° dissolved 1.31 g. of the ester. It was infinitely soluble in ether, benzene and ethanol. It dissolved 34% of its own weight of nitrocellulose (viscosity, 1/2 second), forming a viscous, greenish paste; and 25% of its own weight of cellulose acetate (Celanese satin), forming a viscous, transparent, colorless paste.

**Attempted Oxidation.**—The oxidation of furfuryl formate should be of interest, since the formyl group might be expected to undergo elimination during the process, simultaneously influencing the nature of the reaction of the remainder of the molecule. In an initial attempt to investigate this, furfuryl formate (0.45 mole) was added dropwise to 1.35 moles of hydrogen peroxide (30% aqueous solution) containing a trace of ferrous sulfate. The mixture was stirred vigorously for one hour at room temperature, and then for two hours at 50°; at the end of this time, no odor of the ester could be detected. Formic acid (36% of the theoretical) and furfural (18% of the theoretical) were identified among the diverse products of the reaction; identification of other products was incomplete.

**Preparation and Properties of a Resin.**—Recent work<sup>7</sup> on the use of synthetic resins for the removal of chlorides and sulfates from aqueous solutions included the observation that several resins prepared from either furfural or furfuryl alcohol, usually by condensation with a diamine, possessed widely varying efficiencies. The present authors prepared, washed, dried and sub-divided a resin by an essentially similar procedure, using furfuryl formate, *m*-phenylenediamine, and hydrochloric acid. The initial reaction was vigorous but not violent. The resultant resin was black and very hard. One gram of it was shaken for three hours at 31° with 250 cc. of water containing 500 p. p. m. of sulfuric acid. There was no decrease in the sulfate ion concentration of the solution.

(6) Zanetti, *THIS JOURNAL*, **47**, 535 (1925).

(7) Schwartz, Edwards and Boudreaux, *Ind. Eng. Chem.*, **32**, 1462 (1940).

**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 Traub<sup>8</sup> 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-

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

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.

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[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 described<sup>1</sup> 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.*<sup>1</sup> 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 ( $CH_3C_6H_4N(BCl_3)_3$ ).**—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).