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**FURFURYL FUROATE****Preliminary Paper**

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In a recent paper, Gilman and Vernon<sup>1</sup> remarked that they had found it impossible to condense furfural to furfuryl furoate, in a way similar to the condensation of benzaldehyde to benzyl benzoate, by using calcium carbide as condensing agent. Attempts have been made by the writer to carry out that condensation, with sodium ethylate and also a solution of sodium in furfuryl alcohol containing presumably sodium furylate,<sup>2</sup> but without success. Furfural behaves in this respect, as in its comparative difficulty of oxidation, quite unlike benzaldehyde. In order to study the matter further it seemed desirable to prepare furfuryl furoate by other methods.

Direct esterification of furfuryl alcohol with furoic (pyromucic) acid by the ordinary methods of esterification cannot be carried out because of the action of mineral acids on furfuryl alcohol. The action of pyromucic anhydride, which it was hoped would be as effective as that of fatty acid anhydrides on furfuryl alcohol,<sup>3</sup> gave only tarry products from which no pure compound could be isolated. Resort was then had to the Schotten-Baumann reaction using furoyl chloride in place of benzoyl chloride. Baum<sup>4</sup> has already shown that furoyl chloride can thus be used, by preparing a large number of furoic acid derivatives by that reaction.

**Preparation.**—One mole of furoyl chloride was added gradually and during constant cooling to a water solution of one and a half moles of furfuryl alcohol and 1.5 moles of potassium or sodium hydroxide, enough water being present to make the concentration of the hydroxide about 15%. The ester separated immediately as a yellowish oil with each addition of furoyl chloride. After the mixture had been frequently shaken for 15 to 20 minutes, when the odor of furoyl chloride had disappeared, the ester was separated, shaken thrice with water, dried and distilled under reduced pressure.

**Properties.**—The ester distilled at first as a yellowish oil, which after two fractionations, was a water-white, viscous liquid having a very faint, pleasant, characteristic odor; b. p., 122° (2 mm.). Under atmospheric pressure it boiled above 350°, with much decomposition. It is insoluble in water or petroleum ether but completely miscible with alcohol, ether, benzene and chloroform.

**Dimorphism of Furfuryl Furoate.**—When cooled in a freezing mixture the ester solidified to a white crystalline mass. When the crystallization was watched under the microscope the crystals first appeared as long,

<sup>1</sup> Gilman and Vernon, *THIS JOURNAL*, **46**, 2578 (1924).

<sup>2</sup> The action of sodium on furfuryl alcohol will be the subject of a subsequent communication.

<sup>3</sup> *THIS JOURNAL*, **47**, 535 (1925).

<sup>4</sup> Baum, *Ber.*, **37**, 2949 (1904).

slender prisms, sometimes truncated by what appeared to be octagonal planes, which gradually grew into a transparent mass, in which the crystal forms could not be easily distinguished. These crystals melted at  $19.5^{\circ}$  and were repeatedly obtained by alternate warming and cooling. On standing overnight they passed into an allotropic form melting at  $27.5^{\circ}$ . This form crystallized in short, thick prisms, often twining to form thick, hexagonal plates. It can be melted and caused to crystallize into the  $19.5^{\circ}$  form by observing extreme precautions to prevent seeding. The latter ( $19.5^{\circ}$ ) form is the unstable form, as by seeding the mixture of its solid phase and liquid in a test-tube with a thermometer in the mixture the temperature rises to the melting point of the stable form. In either case the crystallization is very slow, and the liquid phase can be supercooled to  $-10^{\circ}$  before crystals begin to appear.

The density of the supercooled liquid at  $20^{\circ}$  was found to be 1.2443.

*Anal.* Subs., .1729:  $H_2O$ , .0685;  $CO_2$ , 0.3993. Calcd. for  $C_{10}H_8O_4$ : C, 62.50; H, 4.16. Found: C, 62.98; H, 4.43.

**Hydrolysis of the Ester.**—The ester is not readily hydrolyzed by boiling with aqueous potassium hydroxide, probably because of its insolubility in water. The hydrolysis was, however, readily accomplished by using potassium hydroxide dissolved in 40% alcohol and boiling for a few minutes. The solution was diluted with water and extracted several times with ether, the extract dried and evaporated on the water-bath. The residue was identified as furfuryl alcohol by its boiling point,  $169-170^{\circ}$ . The water solution was then acidified with hydrochloric acid, when furoic acid crystallized, being identified by its characteristic odor and its melting point,  $131^{\circ}$ .

### Summary

1. Furfuryl furoate has been synthesized and its properties reported.
2. The ester was shown to be dimorphous, existing in two solid phases melting at  $19.5^{\circ}$  and  $27.5^{\circ}$ , respectively.

Further work upon this compound is now in progress in this Laboratory.

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