

involve an error more serious than those from other sources in such procedures.

Improvements in the procedure will be necessary to give definite information as to the course of hydrolysis of starch.

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## CELLULOSE FUROATE<sup>1,2</sup>

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The increasing industrial importance of cellulose esters presents an attractive field of investigation for new derivatives with desirable properties. One ester which has many desirable properties but which has not been used to any extent because of its excessive cost is cellulose benzoate. The great similarity of furoic acid<sup>3</sup> to benzoic acid made it desirable to prepare cellulose furoate with the hope that it would exhibit the same desirable properties as the benzoate. The recent extensive commercial development of furfural from which the acid can be readily obtained seemed to offer possibilities of obtaining this ester more cheaply than the corresponding benzoate derivative. This ester would be an "all cellulose" ester since furfural can be produced by distilling oxycellulose with dilute hydrochloric acid.

### Discussion of Results

The preparation of furoic acid esters of cellulose was accomplished by means of a modified Schotten-Baumann reaction such as had been employed in the preparation of cellulose benzoate.<sup>4</sup> Tetrachloroethane was used as the diluent. Two types of products seemed to be formed as in the case of cellulose acetate, fibrous esters amounting to 65% of the theoretical and analyzing from 2.5 to 3 furoate residues per C<sub>6</sub> unit, and soluble, black, furoylated degradation products analyzing more than three furoate residues. This investigation was restricted mainly to the former product. The fibrous ester was always colored, varying in shade from light yellow to dark brown, and was insoluble in all the usual solvents for cellulose esters.

<sup>1</sup> Abstracted from a thesis by Kenneth A. Kobe presented to the Faculty of the Graduate School of the University of Minnesota in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering in June, 1928.

<sup>2</sup> Presented before the Cellulose Division of the American Chemical Society at the 78th meeting, Minneapolis, Minnesota, September 9-13, 1929.

<sup>3</sup> Frankland and Aston, *J. Chem. Soc.*, 79, 515 (1901); Hill and Palmer, *Proc. Am. Acad. Arts Sci.*, 23, 188 (1888); Baum, *Ber.*, 37, 2949 (1904).

<sup>4</sup> Cross and Bevan, *ibid.*, 34, 1514 (1901); *Chem. News*, 61, 87 (1890); Cross, Bevan and Beadle, *J. Chem. Soc.*, 63, 838 (1893); Wohl, *Z. angew. Chem.*, 16, 285 (1903); Ost and Klein, *ibid.*, 26, 437 (1913); German Patent 139,669.

The saponification values were obtained by the method of Cross and Bevan as modified by Woodbridge.<sup>5</sup> Analyses show that one acid residue is much more firmly bound than are the other two. This is in accord with the present accepted structure<sup>6</sup> of the hexose residues in cellulose, which show one primary and two secondary alcoholic hydroxyl groups. When the fibers stood for twenty-four hours with standard sodium alcoholate solution, only two furoate groups were removed, while on standing for seven days or refluxing for four hours all groups were removed. It was necessary to make a correction for increase of acid value due to decomposition of the furoic acid.

### Experimental

**Materials.**—The cellulose was standard cellulose. The pyridine was of C. P. quality and was used without further purification. The furoyl chloride, tetrachloroethane and butyl acetate were technical grades and were redistilled before use.

**Method.**—Two grams of cellulose was covered with 100 cc. of diluent, usually tetrachloroethane, and the pyridine and furoyl chloride then added. The flask was attached to a reflux condenser and placed in a paraffin-bath which was heated so that the solvent just boiled. It was usually allowed to heat for three hours and then cooled. The contents of the flask were poured onto a Büchner funnel and the fibers were sucked dry, then washed with chloroform and with alcohol. The fibers were boiled in several portions of water to remove any traces of solvent or reagents. They were sucked dry and all water removed in an oven at 100°. The material in solution was precipitated with petroleum ether, boiled with water and dried.

The maximum yield of fibers (3.6 g. = 65.7%) was secured with 15 cc. each of pyridine and furoyl chloride (2.6 times the theoretical), using 100 cc. of tetrachloroethane as the diluent and heating for three hours. Excess pyridine causes the fibers to lose tensile strength and become dark brown in color; excess furoyl chloride causes a lowered yield. When butyl acetate was used as a solvent, a horn-like mass having a very low saponification value was obtained. Heating for longer periods of time causes a decreased yield of fibers and an increased yield of soluble material of which 1.3 g. was obtained by heating for twenty-four hours while but 0.2 to 0.3 g. forms in the three-hour period.

**Analysis of Product.**—The fibers were rubbed through a 10-mesh screen and mixed to give a uniform sample. A 0.3-g. sample was covered with 50 cc. of an alcohol solution of sodium alcoholate and allowed to stand for twenty-four hours, seven days or refluxed for four hours. The excess alkali was titrated using thymol blue as the indicator. When furoic acid was heated with sodium alcoholate solution for four hours, the acid value increased from 99.1 to 105.3% so that a correction was made in all samples treated in this manner.

Expt.	Stand 24 hrs., %	Reflux 4 hrs., %	Reflux corrected, %	Acid groups per C <sub>6</sub> unit
16	57.6	70.1	66.0	2.2
17	62.4	71.1	67.0	2.3
18	59.3	69.2	65.1	2.1
19	65.2	74.4	74.4	2.9
20	59.5	70.5	70.5	2.5

<sup>5</sup> Woodbridge, *THIS JOURNAL*, 31, 1067 (1909).

<sup>6</sup> Hibbert, *J. Ind. Eng. Chem.*, 13, 256, 334 (1921).

The 1.3 g. of soluble material gave 82.2% furoic acid on standing for twenty-four hours with the sodium alcoholate solution (values from other experiments were 83.5 and 81.6%).

Calculated saponification values: trifuroate,  $C_6H_7O_2(OOCC_4H_5O)_3 = 75.75\%$  of  $C_4H_5O_2COOH$ ; difuroate,  $C_6H_5O_3(OOCC_4H_5O)_2 = 64.0\%$ .

### Summary

1. Cellulose di- and trifuroates have been prepared by treating standard cellulose with furoyl chloride in the presence of pyridine. The esters were fibrous, dark colored and insoluble in the usual solvents for cellulose esters.

2. A considerable degradation of cellulose takes place during the reaction with the production of furoylated degradation products of cellulose which are black amorphous substances.

3. The analysis of cellulose trifuroate by saponification shows very clearly the fundamental difference of two of the alcoholic hydroxyl groups in the hexose residue from the third or primary hydroxyl and thus confirms the present accepted structure of the hexose residue.

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## SOME HETEROCYCLIC DERIVATIVES OF DIPHENYL

BY J. M. F. LEAPER

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The production on a large scale of diphenyl in order to supply the demand for this very useful heat-transfer medium has already resulted in the price of this material being brought down to a figure comparable with that of any of the polynuclear hydrocarbons, except naphthalene.

Its applications in the chemical industry for synthetic purposes are in consequence destined to become of increasing importance, especially as it appears likely that the price can be further reduced.

The recent work by Jenkins, McCullough and Booth<sup>1</sup> has indicated for instance that the simple mono-chloro, nitro and amino derivatives can be produced readily on a commercial basis, and the work of C. H. Penning<sup>2</sup> has extended the knowledge of the polychlorinated derivatives.

The present paper covers some new heterocyclic compounds derived from 4-amidodiphenyl, the derivatives chosen for study being such as might be expected to be of possible commercial application in the rubber industry, in froth flotation of ores, as inhibitors in steel pickling or in dyestuff manufacture.

Use has been made in this work of the method described by R. Herz<sup>3</sup> for introducing sulfur into the ring by the action of sulfur chloride on the

<sup>1</sup> Jenkins, McCullough and Booth, *Ind. Eng. Chem.*, **22**, 31 (1930).

<sup>2</sup> Penning, *ibid.*, **22**, 1180 (1930).

<sup>3</sup> Herz, German Patent 360,690.