**α,β-Diphenyl-β-benzhydryl-ethenyl *p*-Bromobenzoate. XXII.**—To a solution of phenylmagnesium bromide from 0.8 g. of magnesium was added 8.4 g. of finely powdered benzal desoxybenzoin. The mixture was boiled for twenty minutes, then treated with 7.5 g. of freshly distilled *p*-bromobenzoyl chloride and boiled again for two hours. The usual manipulations gave a product which was sparingly soluble in ether and in alcohol, which crystallized in prisms, and which melted at 183°.

*Anal.* Calcd. for $C_{34}H_{25}O_2Br$: C, 74.8; H, 4.6. Found: C, 74.7; H, 4.7.

**Hydrolysis.**—The ester on hydrolysis with dilute methyl alcoholic potassium hydroxide gave but two products: triphenyl propiophenone and *p*-bromobenzoic acid.

## Summary

1. The magnesium derivatives which are formed by the addition of Grignard reagents to those α,β-unsaturated ketones which have no substituents in the alpha position behave like the enolates of β-ketonic esters; like these enolates they combine with unsaturated ketones and with other substances that have sufficiently active carbonyl groups. The reaction with acid chlorides results in the formation of C-acyl derivatives.

2. The magnesium derivatives which are formed by adding Grignard reagents to α,β-unsaturated ketones which have hydrocarbon residues in the alpha position, combine neither with unsaturated ketones nor with aldehydes; they therefore do not form secondary products. The reaction between these magnesium derivatives and acid chlorides results in the formation of O-acyl derivatives.

CONVERSE MEMORIAL LABORATORY
CAMBRIDGE, MASSACHUSETTS

RECEIVED JULY 26, 1932
PUBLISHED MARCH 7, 1933

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# Furan Reactions. IV. Furoic Acid from Furfural

BY CHARLES D. HURD, J. W. GARRETT[1] AND E. N. OSBORNE[1]

In the Cannizzaro reaction with furfural, mineral acids cannot be used to neutralize the excess of alkali without resinifying the furfuryl alcohol which is formed. Hence, it is customary[2] to extract the latter with ether before acidification. In the method proposed, the excess of alkali is neutralized with furoic acid and the furfuryl alcohol separated directly, thus making the method suitable for large scale use. Also, the excess of alkali may be omitted altogether with yields only slightly lower.

The direct oxidation of furfural to furoic acid by means of potassium dichromate and sulfuric acid has also been studied and a satisfactory method developed. The manganous salt of furoic acid was synthesized. It was found to crystallize with three molecules of water.

---

(1) Holders of Quaker Oats Fellowships, administered through the Miner Laboratories, Chicago.

(2) Wilson, "Organic Syntheses," John Wiley and Sons, New York, 1926, Vol. VI, p. 44.

## Experimental Part

**The Cannizzaro Reaction.**—Following the direction of "Organic Syntheses,"[2] 1 kg. (10.4 moles) of redistilled furfural and 820 g. of 33% sodium hydroxide solution (6.9 moles of sodium hydroxide) were used to bring about the Cannizzaro reaction. To remove the excess 1.7 moles of alkali at the conclusion of the reaction, 1.8 moles (200 g.) of furoic acid[3] was added directly to the mixture and the mass stirred well. The mixture was cooled to 0° and pressed as dry as possible on a suction filter. The solid was transferred to a beaker, triturated therein with a 200–250 cc. portion of cold water, cooled to −5° and again sucked dry. The trituration of the solid with water was repeated.

The combined filtrates were distilled at 25 mm. nearly to dryness using a heating bath, the temperature of which was kept below 145°. Water was removed from this distillate by vacuum distillation from a special Claisen flask equipped with a water-cooled head.[4] When the water had been distilled away, the residue of furfuryl alcohol was thrice shaken with saturated sodium bisulfite solution to remove any furfural present. The furfuryl alcohol was fractionated under reduced pressure (83° at 24 mm.); yield, 367–390 g., or 72–76%. The refractive index, $n^{21}_{D}$, was 1.4869.

All the solid residues were dissolved in warm water and filtered from a small amount of dark, insoluble material. The filtrate was acidified with concd. hydrochloric acid, cooled to 0° and filtered. The solid was washed twice with a little ice water and then dried. Yields of 420–440 g. (73–76%) of white furoic acid were obtained in excess of the 200 g. which was also recovered. The ash content of the furoic acid in this stage of purity was 1.5%, weighed as the sulfate.

If a slight deficiency of alkali was used at the outset (5.0 moles of sodium hydroxide for each 10.4 moles of furfural), good results were obtained also. In this case the reaction mixture was filtered and worked up directly without adding any furoic acid. Otherwise an identical procedure was followed. The yields of furfuryl alcohol were about the same as the above, whereas the yields of furoic acid were about 5% less.[5]

**Manganous Furoate Trihydrate,** $(C_4H_3O—COO)_2Mn3\cdot H_2O$.—Twenty-eight grams (0.25 mole) of furoic acid was dissolved in a minimum quantity of hot water (about 125 cc.) and then 15 g. (0.13 mole) of solid manganous carbonate was added slowly. The mixture was stirred and heated until the evolution of carbon dioxide had ceased. The slight excess of manganous carbonate was filtered off and the filtrate was concentrated to a thick sirup which possessed a light brown color. When cool, crystallization was induced by scratching. The dark pink crystals weighed 23.6 g.; yield, 68.1%.

The product was dissolved in a small portion of hot water. Slow evaporation at about 50° with seeding gave large crystals. The sample used for determination of water of crystallization was dried in a desiccator over calcium chloride. Then the water was driven off at 105°. In the analysis for manganese, the sample was dried for three hours at 105° to constant weight.

*Anal.* Subs., 1.9712; $H_2O$, 0.3173. Calcd. for $(C_4H_3O—COO)_2Mn\cdot 3H_2O$: $H_2O$, 16.33. Found: $H_2O$, 16.20. Subs., 0.6535: $Mn_3O_4$, 0.1790. Calcd. for $(C_4H_3O—COO)_2Mn$: Mn, 19.81. Found: Mn, 19.73.

Manganous furoate was found to be very soluble in hot and cold water, soluble in ordinary ethyl alcohol, insoluble in absolute alcohol, carbon tetrachloride and acetone. The anhydrous salt begins to decompose at about 290°.

---

(3) It was found that ammonium sulfate could also be used satisfactorily in this neutralization.

(4) This was of the Clarke and Rahrs type [*Ind. Eng. Chem.*, **15**, 349 (1923)] but any efficient column would be satisfactory.

(5) From experiments with Mr. W. A. Whittier. Dr. F. N. Peters, Jr., of the Quaker Oats Co. Chemical Laboratory has found this method suitable for runs nine times the size of the one described. He recommended a combination of salting-out (by sodium chloride) and distillation rather than distillation alone to remove the furfuryl alcohol from its aqueous solution.

**Oxidation of Furfural.**—After several experiments with temperature and time and dilution as the variables, the following conditions seemed to give the best yields in this oxidation.

In a round-bottomed liter flask which was equipped with a mechanical stirrer, dropping funnel and reflux condenser, were placed 100 g. of furfural, 100 g. of potassium dichromate and 10 g. of water. The flask was then heated to 100° on a steam-bath and, dropwise, there was added a mixture of 200 g. of sulfuric acid and 100 g. of water during thirty to forty-five minutes. The heat of reaction was such that the steam-bath was removed after a short time. When complete, the reaction mixture was cooled and nearly neutralized with sodium hydroxide. Then it was completely neutralized with sodium carbonate. The chromium hydroxide which was filtered off weighed 56 g. after drying. The filtrate was made acid with sulfuric acid and the dark brown precipitate of furoic acid was collected upon a filter. The filtrate was concentrated for more furoic acid. In all, 105 g. of crude material was formed. It was dissolved in the minimum amount of hot water, filtered from any insoluble matter, and the filtrate cooled. Eighty-seven grams (dry) of white furoic acid separated; yield, 75% The crystals melted at 131.5°.

## Summary

A method is given for the oxidation of furfural to furoic acid by potassium dichromate and sulfuric acid. Improved directions are recorded for the preparation of furfuryl alcohol and furoic acid from furfural by the Cannizzaro reaction. Manganous furoate trihydrate is described.

EVANSTON, ILLINOIS

RECEIVED AUGUST 3, 1932
PUBLISHED MARCH 7, 1933

---

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE UNIVERSITY, EDGBASTON, BIRMINGHAM, ENGLAND]

# Sucrose and Other Disaccharides. Sir James Irvine's "Correction"

BY H. C. CARRINGTON, W. N. HAWORTH AND E. L. HIRST

In a recent paper which deals with the properties of 2,3,6-trimethylglucose and their bearing on the chemistry of the di- andpoly saccharides, Irvine and McGlynn[1] revert to a theme which was initiated and decided by one of us, but in their treatment of the subject they again dispense with the isolation of crystalline reference substances. They describe 2,3,6-trimethyl-$\gamma$-gluconolactone as a liquid with an initial rotation, $[\alpha]_D$ $+80.5°$ or 90.5° (both values being given), observed in a mixture of alcohol and water of unspecified composition. As shown in our experimental section the pure lactone is a crystalline substance, m. p. 29–30°, with the initial rotation $[\alpha]_D$ $+55°$ in water, alcohol or mixtures of the two solvents. We have characterized it as a $\gamma$-lactone by measuring its rate of mutarotation in water (which Irvine and McGlynn omitted to attempt), by preparing from it the crystalline phenylhydrazide of 2,3,6-trimethylgluconic

---

(1) Irvine and McGlynn, THIS JOURNAL, **54**, 356 (1932).