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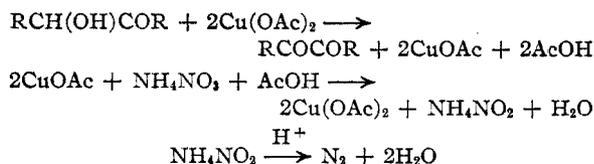
## The Catalytic Oxidation of Benzoin to Benzil

BY MARVIN WEISS AND MILDRED APPEL

Since the first observation over one hundred years ago, that benzoin could be oxidized to benzil by the use of chlorine<sup>1</sup> or nitric acid,<sup>2</sup> many other procedures have been developed. Of these, the use of copper sulfate and pyridine as a modified Fehling solution,<sup>3,4</sup> which may be regenerated by air, is of recent interest. Earlier a catalytic method had been reported using copper oxide at high temperatures.<sup>5</sup> In 1951, Bacharach and Brolles, Jr.,<sup>6</sup> attempted the nitration of benzoin using lithium nitrate in acetic anhydride and unexpectedly obtain benzil in poor yields. These yields were improved, somewhat, by the addition of cupric nitrate. Independently, in 1941, during a study of the action of ammonium salts in glacial acetic acid, it was found that a smooth conversion of benzoin to benzil could be achieved by the use of a large excess of ammonium nitrate, which, however, did not react completely when over 0.5 mole of benzoin was used.<sup>7</sup>

A satisfactory preparative method has now been found to oxidize benzoin and other acyloins to the corresponding diketones in 90% to quantitative yields, by the use of a catalytic amount of a cupric salt, which may be regenerated internally by ammonium nitrate. Since this reaction is run in acetic acid, the solvent performs a dual role by decomposing the formed ammonium nitrite, while serving as an excellent medium to crystallize the diketones. The reaction may be fairly specific for  $\alpha$ -hydroxy ketones, since neither benzaldehyde, nor benzohydrol nor mandelic acid is oxidized under these conditions. Iron, cobalt and nickel salts have been found to act equally well as catalysts.

The general reaction may be written as



That the reaction proceeds as outlined is evidenced by the facts: that in molar quantities ammonium nitrate converts only 40% of pure benzoin to benzil, while in the presence of a catalytic amount of cupric acetate a quantitative yield is obtained. When cupric acetate is used alone, the greenish blue solution becomes colorless, and a

gradual precipitate of a reddish brown hydrated copper oxide appears. This precipitate may be redissolved by the addition of ammonium nitrate, forming again the greenish blue solution. At the start of the reflux period, there is a brisk and copious evolution of a colorless and neutral gas (nitrogen), which continues until the reaction is complete.

## Experimental

**Benzil (small run).**—In a 100-cc. flask fitted with a reflux condenser are placed 0.1 g. (0.0005 mole) of cupric acetate, 5 g. (0.0625 mole) of ammonium nitrate, 10.6 g. (0.05 mole) of benzoin and 35 cc. of an 80% by volume acetic acid-water solution. The mixture is heated with occasional shaking. When solution occurs, a vigorous evolution of gas commences. After refluxing one and a half hours, the solution is cooled and seeded with a crystal of benzil. After crystallization is complete, additional water is added to the flask to precipitate the remaining benzil. The benzil is filtered with suction and washed well with water. The yield is 10.5 g. or quantitative, m. p. 95°; Fehling test negative.

**Benzil (large run).**—In a five-liter flask equipped with two reflux condensers and an oil-sealed stirrer are placed 636 g. (3 moles) of crude benzoin,<sup>8,9</sup> 300 g. (3.75 moles) of ammonium nitrate,<sup>10</sup> 6 g. of cupric acetate (0.03 mole) and 2100 cc. of 80% acetic acid by volume. The mixture is heated with continuous stirring. When solution results, the stirring is discontinued, allowing the vigorous evolution of nitrogen to proceed. The speed of the reaction may be checked by external cooling. The solution is refluxed for one and a half hours, cooled to 70° and seeded with a crystal of benzil. Stirring is started again until crystallization is complete. The benzil is filtered with suction and washed with 200 cc. of 80% acetic acid. The filtrate and washings are reserved for a second batch. The benzil is then washed well with water and dried. The yield is 560 g. or 90%, m. p. 94–95°.

A second charge of benzoin and ammonium nitrate is added to the reserved filtrate and reacts as above. The yield of benzil is 625 g. or 100%, m. p. 93–94°. Dilution of the filtrate will yield additional benzil.<sup>11</sup>

**Anisil, *o*-Veratril and Futil.**—These compounds were prepared in a manner similar to benzil. These results are presented in tabular form.

Piperil could not be prepared from piperoin due to the formation of intractable tars. This is not surprising since piperil cannot be prepared from piperoin with nitric acid.<sup>12</sup>

**Determination of Benzoin in Benzil-Benzoin Mixtures.**—A convenient separation method is based upon the catalytic cleavage of benzil by sodium cyanide, which does

(8) "Organic Syntheses," Coll. Vol. I, John Wiley & Sons, Inc., New York, N. Y., 1941, p. 94.

(9) The wet cake may be used directly, provided all the sodium cyanide is washed out and the water content approximated. The final acetic acid concentration must be over 70% by volume.

(10) A slight excess of ammonium nitrate over the theoretical amount is needed, since impurities in the benzoin cause more than one mole to be used. However, with pure benzoin only equimolar quantities are necessary.

(11) In view of a recent discussion involving an explosion of a cobaltinitrite solution which had been concentrated, and which contained some of the same ions present in the experiments above, a word of caution is inserted. However, no difficulty was experienced in the many experimental variations tried. For bibliography see Horowitz, *Anal. Chem.*, **20**, 89 (1948).

(12) Perkin, *J. Chem. Soc.*, **59**, 164 (1891).

(1) Laurent, *Ann.*, **17**, 91 (1836).  
 (2) Zinin, *ibid.*, **34**, 188 (1840).  
 (3) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 87.  
 (4) U. S. Patent 2,377,749 (1945).  
 (5) Zetsche and Zala, *Helv. Chim. Acta*, **9**, 288 (1926).  
 (6) Bacharach and Brolles, Jr., *Rec. trav. chim.*, **50**, 732 (1931).  
 (7) Klein, *THIS JOURNAL*, **63**, 1474 (1941).

TABLE I

Substance	Used, g.	Cu-(OAc) <sub>2</sub> , g.	NH <sub>4</sub> -NO <sub>2</sub> , g.	80% Acetic acid, cc.	Diketone, M. p., °C.	Yield, %
Benzoin	10.6	0.1	5.0	35.0	95	100
Anisoin	2.04	.015	0.75	7.5	132	97
<i>o</i> -Veratrin	1.66	.1	0.5	10.0	146	98
Furoin	1.92	.2	1.0	30.0	165	91

<sup>a</sup> All melting points are of the products as formed without further purification, and corrected for the emergent stem.

not affect the benzoin. To 2.00 g. of a mixture of equal quantities of benzil and benzoin dissolved in 45 cc. of ethanol, a solution of 0.1 g. of sodium cyanide in 5 cc. of water is added, and shaken for ten minutes. Five grams of sodium bisulfite dissolved in 50 cc. of water is then added and the precipitated benzoin filtered and dried; recovered, 1.00 g., m. p. 135° (cor.).

Anisil and *o*-veratril (2,3,2'3'-tetramethoxybenzil) were checked by sodium cyanide cleavage. The acids that

formed showed no melting point depression when mixed with corresponding acids obtained by oxidation of the aldehydes. Furoil showed no melting point depression when mixed with furoil obtained by another method.<sup>8</sup>

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### Summary

1. A convenient method is described for the oxidation of  $\alpha$ -hydroxy ketones to diketones by the use of catalytic amounts of copper, iron, nickel and cobalt salts, which are regenerated continuously by means of ammonium nitrate.

2. The ammonium nitrite formed is decomposed by the acetic acid allowing pure diketones to crystallize.

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## Reaction of Mercaptans with Unsaturated Compounds

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In recent articles by Rapoport, Smith and Newman<sup>2</sup> and Hurd and Gershbein<sup>3</sup> the addition of mercaptans to unsaturated compounds is reported. We wish to report (Table I) work of a similar nature carried out in this Laboratory over the past few years. We have found this reaction to be generally applicable to the facile preparation of a wide variety of unsymmetrical sulfides.

Comparing catalysts for the addition of benzyl mercaptan to ethyl acrylate in dioxane as solvent, aqueous and methanolic sodium hydroxide solutions were found unsatisfactory since gels formed before all of the acrylate had been added (yields 75 and 78%, respectively). Triton B<sup>4</sup> gave the best yield (94%) followed closely by anhydrous potassium carbonate and tetra-(2-hydroxyethyl)-ammonium hydroxide.

Comparing solvents with triton B catalyst, benzene was more satisfactory than dioxane as the catalyst could be washed out with small amounts of water (yield 90%). Ethanol was also tried but was inferior (yield 62%).

The addition of mercaptans to unsaturated aldehydes may take at least two courses. In the case of ethyl mercaptan and crotonaldehyde addition took place at the double bond. However, the reaction between benzyl mercaptan and cinnamaldehyde took a different course. The first fraction on distillation proved to be cinnamaldehyde dibenzyl mercaptal. This was shown by the fact

that it did not yield a dinitrophenylhydrazone and on distillation in the presence of traces of acid it yielded benzyl mercaptan; the large residue was not identified.

A dioxane solution of octene and octyl mercaptan in the presence of triton B<sup>4</sup> at room temperature gave only a small yield of dioctyl sulfide in a two-hour reaction period. The reaction was not further studied but the yield can undoubtedly be improved by raising the temperature and increasing the time. Isosafrole behaved similarly.

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### Experimental

Triton B, acrylonitrile, methyl and ethyl acrylates were obtained through the courtesy of Dr. E. H. Riddle, Rohm & Haas Co., to whom we are grateful. The methyl vinyl ketone was obtained through the courtesy of du Pont. The thioglycol and tetra-(2-hydroxyethyl)-ammonium hydroxide were obtained from Carbide and Carbon, while the other compounds were Eastman Kodak Co. products. All were used without purification or removal of antioxidants.

The compounds described here were prepared as follows: one mole of the mercaptan was dissolved in 200 cc. of solvent and 10 g. of the catalyst was then added. To this mixture one mole of the unsaturated compound was then added with stirring in small portions so as to control the temperature. In the case of methyl and ethyl mercaptans, the temperature was kept below the boiling point of the mercaptan. In the addition of ethyl mercaptan to ethyl acrylate and to vinyl acetate, the temperature reached 55 and 45°, respectively, so rapidly that difficulty was experienced in cooling the reaction unless it was precooled, while with benzyl mercaptan the temperature was kept below

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(2) Rapoport, Smith and Newman, *THIS JOURNAL*, **69**, 693 (1947); see references 2 and 3 for a brief bibliography.

(3) Hurd and Gershbein, *ibid.*, **69**, 2328 (1947).

(4) An approximately 35% solution of benzyltrimethylammonium hydroxide.