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 or nitric acid, many other procedures have been developed. Of these, the use of copper sulfate and pyridine as a modified Fehling solution, which may be regenerated by air, is of recent interest. Earlier a catalytic method had been reported using copper oxide at high temperatures. In 1931, Bacharach and Brolles, Jr., attempted the nitration of benzoin using lithium nitrate in acetic anhydride and unexpectedly obtain benzil in poor yields. These results 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 would not react completely when over 0.5 mole of benzoin was used.

A satisfactory preparatory method has now been found to oxidize benzoin and other acyclics 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 α-hydroxy ketones, since neither benzaldehyde, nor benzoylhydroxyl 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:

\[ \text{RCH(OH)COR} + 2\text{Cu(OAc)}_2 \rightarrow \text{RCOCOR} + 2\text{CuOAc} + 2\text{HAc} \]

\[ 2\text{CuOAc} + \text{NH}_4\text{NO}_2 + \text{AcOH} \rightarrow 2\text{CuO(OAc)}_2 + \text{NH}_3\text{NO}_2 + \text{H}_2\text{O} \]

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, 1 g. (0.0025 mole) of ammonium nitrate, 10.6 g. (0.05 mole) of benzoin and 55 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. 96°; Fehling test negative.

Benzil (large run).—In a five-liter flask equipped with two reflux condensers and an oil-sealed stirrer are placed 650 g. (5 moles) of crude benzoin, 300 g. (3.75 moles) of ammonium nitrate, 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 crystallisation is complete. The benzil is filtered with suction and washed with 700 cc. of 30% 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 850 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 655 g. or 100%, m. p. 95-96°. Dilution of the filtrate will yield additional benzil.

Antisol, o-Veratral and Furl.—These compounds were prepared in a manner similar to benzil. These results are presented in tabular form.

Piperil could not be prepared from piperoxin due to the formation of intractable tar. This is not surprising since piperil cannot be prepared from piperoxin with nitric acid.

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

(1) Laurent, Ann., 17, 91 (1860).
(2) Zincke, ibid., 84, 189 (1864).
(5) Heyl, private communication (1939).
(6) Bacharach and Brolles, Jr., J. Rec. chem. soc., 80, 725 (1931).
Reactions of Mercaptans with Unsaturated Compounds

By J. Lester Seabo and Eric T. Stiller

In recent articles by Rapoport, Smith and Newman and Hurd and Gershein 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 the acrylate had been added (yields 75 and 78%, respectively). Triton B4 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 mercaptal; the large residue was not identified.

A dioxane solution of octene and octyl mercaptan in the presence of triton B 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. Isoasafrole 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 thioglycolic 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. This mixture was cooled to 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°C, 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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Table I

<table>
<thead>
<tr>
<th>Substance</th>
<th>Benzyl</th>
<th>Anisoin</th>
<th>o-Veratraldehyde</th>
<th>Furfural</th>
<th>Di-nesethanolamine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Use</td>
<td>NO₃</td>
<td>C₆H₅NO₂</td>
<td>C₆H₅NO₂</td>
<td>C₆H₅NO₂</td>
</tr>
<tr>
<td></td>
<td>g.</td>
<td>g.</td>
<td>g.</td>
<td>g.</td>
<td>g.</td>
</tr>
<tr>
<td>Benzoin</td>
<td>10.6</td>
<td>0.1</td>
<td>5.0</td>
<td>35.0</td>
<td>95</td>
</tr>
<tr>
<td>Anisoin</td>
<td>2.04</td>
<td>0.15</td>
<td>0.75</td>
<td>7.5</td>
<td>132</td>
</tr>
<tr>
<td>o-Veratraldehyde</td>
<td>1.66</td>
<td>0.1</td>
<td>0.5</td>
<td>10.0</td>
<td>146</td>
</tr>
<tr>
<td>Furfural</td>
<td>1.92</td>
<td>2</td>
<td>1.0</td>
<td>30.0</td>
<td>165</td>
</tr>
</tbody>
</table>

* All melting points are of the products as formed without further purification, and corrected for the emergent stem. Not affect the benzoin.

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

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

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[Contribution from the Organic Laboratory of the Wyeth Institute of Applied Biochemistry]

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(1) Present address: Squibb Institute for Medical Research, New Brunswick, New Jersey.
(3) Hurd and Gershein, ibid., 69, 2328 (1947).
(4) An approximately 35% solution of benzyldimethylammonium hydroxide.