Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at http://www.nap.edu/catalog.php?record_id=12654). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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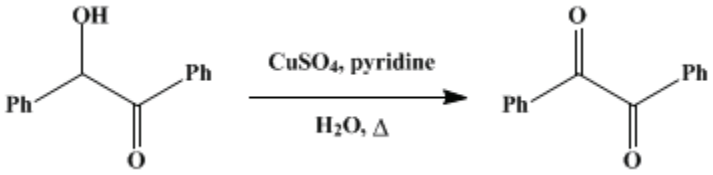
Organic Syntheses, Coll. Vol. 1, p.87 (1941); Vol. 6, p.6 (1926).

BENZIL



Submitted by H. T. Clarke and E. E. Dreger.
Checked by Roger Adams and Gerald H. Coleman.

1. Procedure

In a 12-l. flask, fitted with a mechanical stirrer and mercury seal, a reflux condenser and an inlet tube for the introduction of air, is placed a mixture of 4100 g. (16.4 moles) (Note 1) of crystalline copper sulfate (Note 2), 4000 g. of technical pyridine and 1600 g. of water. This is heated on a steam bath with stirring until the copper sulfate is completely dissolved and then 1696 g. (8 moles) of benzoin (p. 94; unrecrystallized material is satisfactory) is added and heating and stirring continued for two hours. The reaction mixture becomes dark green in color and the melted benzil forms the upper layer. After cooling, the copper sulfate-pyridine solution is decanted and the benzil washed with water and then heated with 3–4 l. of 10 per cent hydrochloric acid. After cooling, the benzil is filtered, washed with water, dried and recrystallized from carbon tetrachloride (2 l. of solvent per kg. of benzil). By concentration of the mother liquors a certain amount of benzil is always obtained. The total yield is 1450 g. (86 per cent of the theoretical amount) of recrystallized material melting at 94–95° (Note 3).

The copper sulfate-pyridine mixture is readily reoxidized by passing a current of air through it for thirty-six hours (Note 4). To this resulting solution is now added 200 g. of pyridine and it is then used for oxidizing another 1696 g. portion of benzoin.

2. Notes

1. In checking this preparation, runs about 25 per cent of the size described were made. The yields were about 3 per cent less than in the larger runs. For the reoxidization of the smaller amount of copper sulfate-pyridine solution, air was passed through for fifteen hours.
2. Copper hydroxide (or carbonate) does not dissolve in pyridine.
3. In comparing the copper sulfate-pyridine method with the nitric acid method (Org. Syn. **1**, 25) it should be pointed out that the constants on the samples are as follows:

Method	M. P. Crude	M. P. Recryst.	Fehling's Test on Recryst.
Copper sulfate-pyridine.....	94–95°	94–95°	Negative
Nitric acid.....	88°	93–94°	Positive

In other words, by the nitric acid oxidation it is difficult to obtain a product completely free from benzoin. The yields by the nitric acid method are generally about 95–96 per cent, whereas with the copper sulfate-pyridine method the yield drops to approximately 86 per cent.
The melting temperatures of mixtures of benzil and benzoin show[1] that the maximum possible depression is 10°.
4. Fifteen hours was found not long enough to effect a complete oxidation.

3. Discussion

Benzil is readily formed by the oxidation of benzoin with nitric acid,[2] chlorine,[3] iodine,[4] electrolytically[5] and catalytically.[6] The procedure described is based on the observation[7] that benzoin

reduces Fehling's solution in the cold. Pyridine was selected because it prevents precipitation of cuprous oxide, is not so volatile as ammonia, and acts as a partial solvent for benzoin. It has been shown[8] that copper, pyridine and air oxidize benzoin to benzoic acid. The same oxidation also takes place in the absence of copper. Benzil can also be prepared from desoxybenzoin with selenium dioxide.[9]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 496
- Org. Syn. Coll. Vol. 4, 377

References and Notes

1. Vanstone, J. Chem. Soc. **95**, 600 (1909).
2. Zinin, Ann. **34**, 188 (1840); Adams and Marvel, Org. Syn. **1**, 25 (1921).
3. Laurent, Ann. **17**, 91 (1836).
4. Corson and McAllister, J. Am. Chem. Soc. **51**, 2822 (1929).
5. James, ibid. **21**, 893 (1899).
6. Zetzsche and Zala, Helv. Chim. Acta, **9**, 288 (1926).
7. Fischer, Ann. **211**, 214 (footnote) (1882).
8. Mohler, Helv. Chim. Acta, **8**, 740 (1925).
9. Hatt, Pilgrim, and Hurran, J. Chem. Soc. **1936**, 93.

Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

copper sulfate-pyridine

Fehling's solution

Desoxybenzoin

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

nitric acid (7697-37-2)

carbon tetrachloride (56-23-5)

copper sulfate (7758-98-7)

Benzoic acid (65-85-0)

copper (7440-50-8)

iodine (7553-56-2)

Benzil (134-81-6)

pyridine (110-86-1)

Benzoin (119-53-9)

Copper hydroxide (20427-59-2)

chlorine (7782-50-5)

cuprous oxide

selenium dioxide (7446-08-4)