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.

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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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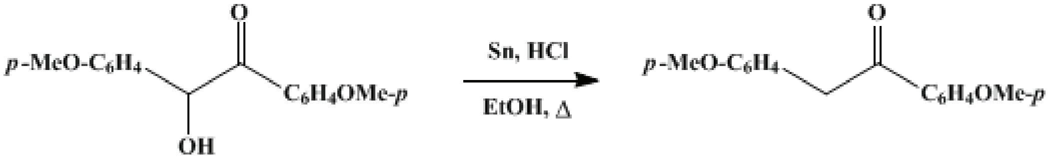
DEOXYANISOIN

[Acetophenone, 4'-methoxy-2-(*p*-methoxyphenyl)-]



Submitted by P. H. Carter, J. Cymerman Craig, Ruth E. Lack, and M. Moyle[1].
Checked by Max Tishler and E. M. Chamberlin.

1. Procedure

A 500-ml. round-bottomed flask, equipped with a reflux condenser, is charged with 40 g. (0.33 mole) of powdered tin (Note 1) and (Note 2), 52 g. (0.19 mole) of anisoin (Note 3), 52 ml. of concentrated hydrochloric acid (Note 4), and 60 ml. of 95% alcohol. After the mixture is refluxed for 24 hours (Note 5), the boiling solution is decanted from undissolved tin, cooled to 0°, and the white crystals are filtered by suction. The filtrate is heated to boiling and then used to wash the tin by decantation. The combined washings are cooled to 0°, and the crystalline solid is collected by suction filtration. Recrystallization of the combined solids from 450 ml. of boiling 95% ethanol (Note 6) and (Note 7) gives, on cooling to 0°, colorless crystals of deoxyanisoin melting at 108–111°. The yield is 42–45 g. (86–92%).

2. Notes

1. A reduction in the amount of tin lowers the yield. Best results are obtained using powdered tin of between 100 and 200 mesh size. Use of tin coarser than 100 mesh results in the presence of unchanged anisoin, while tin finer than 200 mesh tends to conglomerate, causing lower yields. The checkers used tin obtained from E. H. Sargent Co., Chicago, labeled 200 mesh.
2. No advantage is gained by using amalgamated tin.
3. This procedure is generally applicable to the preparation of symmetrical deoxybenzoins. The submitters have prepared (*a*) deoxybenzoin (m.p. 56–58°) in 80–84% yield from 53 g. of benzoin (0.25 mole), 53 ml. of concentrated hydrochloric acid, 50 ml. of 95% alcohol, and 53 g. of powdered tin (0.44 mole), recrystallizing from 160 ml. of boiling 95% alcohol and cooling to 0°; (*b*) deoxypiperoin (m.p. and mixed m.p. 112–114°) in 89% yield from 14.3 g. of piperoin (0.048 mole), 13 ml. of concentrated hydrochloric acid, 30 ml. of 95% alcohol, and 10 g. of powdered tin (0.083 mole), recrystallizing from 140 ml. of boiling 95% alcohol and cooling to 0°.
4. A reduction in the amount of hydrochloric acid lowers the yield.
5. Lower yields are obtained by using reflux periods of 16 or 18 hours.
6. The checkers recommend washing the product with cold 95% alcohol; otherwise the product tends to discolor on standing.
7. Addition of water to the filtrate does not yield any further crystalline products.

3. Discussion

The synthesis of deoxybenzoin from phenacetyl chloride and benzene by the Friedel-Crafts reaction has been described.[2] For symmetrically substituted deoxybenzoins, direct reduction of the readily accessible benzoin is a more convenient method. Reduction of benzoin by zinc dust and acetic acid,[3] and by hydrochloric acid and granulated tin[4,5] or amalgamated powdered tin[6] has been reported. The present method is based on a publication of the authors.[7]

References and Notes

1. Dyson Perrins Laboratory, Oxford, England.
2. C. F. H. Allen and W. E. Barker, *Org. Syntheses*, Coll. Vol. **2**, 156 (1943).
3. E. P. Kohler and E. M. Nygaard, *J. Am. Chem. Soc.*, **52**, 4133 (1930).
4. J. S. Buck and S. S. Jenkins, *J. Am. Chem. Soc.*, **51**, 2163 (1929).
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6. O. A. Ballard and W. M. Dehn, *J. Am. Chem. Soc.*, **54**, 3970 (1932).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

Deoxyanisoin

anisoin

deoxypiperoin

piperoin

phenacetyl chloride

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

tin (7440-31-5)

Benzoin (119-53-9)

zinc (7440-66-6)

deoxybenzoin (451-40-1)

Acetophenone, 4'-methoxy-2-(p-methoxyphenyl)- (120-44-5)