



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.

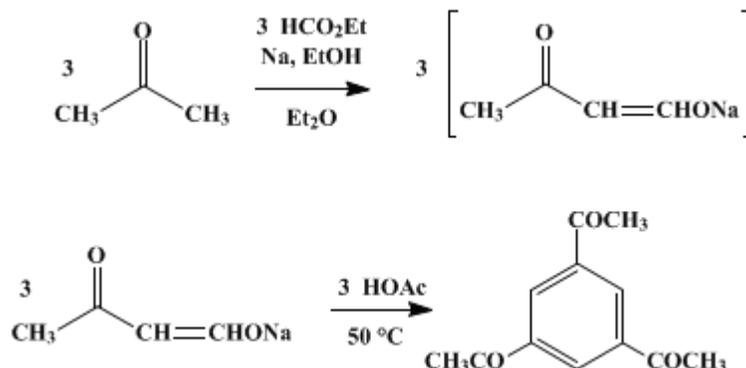
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.829 (1955); Vol. 27, p.91 (1947).

1,3,5-TRIACETYL BENZENE

[Benzene, 1,3,5-triacetyl]



Submitted by Robert L. Frank and Robert H. Varland.
Checked by Arthur C. Cope and W. H. Jones.

1. Procedure

Sixty-nine grams (3.0 gram atoms) of freshly cut **sodium** is placed in a 1-l. round-bottomed flask with 400 ml. of dry **xylene** (Note 1) and heated until all the **sodium** is melted. The flask is closed with a rubber stopper and shaken vigorously to form finely powdered **sodium** (Note 2). When cool, the contents are transferred to a 5-l. three-necked round-bottomed flask, and the **xylene** is decanted. The powdered **sodium** is then washed with two 100-ml. portions of anhydrous **ether** by decantation, after which 1 l. of anhydrous **ether** is added. The flask is placed on a steam bath and fitted with a Hershberg stirrer, an upright condenser, and a 500-ml. dropping funnel. The condenser and funnel are protected from moisture by calcium chloride tubes. Through the dropping funnel is then added with stirring 138 g. (175 ml., 3.0 moles) of absolute **ethanol** at such a rate that gentle refluxing occurs. The mixture is refluxed and stirred for 6 hours after the addition is complete.

The reaction mixture is diluted with 1.5 l. of anhydrous **ether**, and a mixture of 174 g. (220 ml., 3.0 moles) of **acetone** (Note 3) and 222 g. (241 ml., 3.0 moles) of **ethyl formate** (Note 4) is placed in the dropping funnel and added to the flask over a period of 2 hours. Stirring is continued for 2 hours after the **acetone** and **ethyl formate** have been added (Note 5).

The reaction mixture is then rapidly extracted with five 1-l. portions of water (Note 6). **Acetic acid** is added to the water solution until it is acid to litmus. The acidified solution is warmed to 50° on a steam bath and maintained at approximately that temperature for 2 hours. It is subsequently allowed to stand at room temperature for 48 hours, during which time the **triacetylbenzene** crystallizes.

The crude yellow crystalline solid (m.p. in the range 150–162°) is collected on a filter; the yield is 84–94 g. (41–46%). It is recrystallized by dissolving in hot **ethanol** (18 ml. of **ethanol** per gram), adding 2 g. of **Norit**, filtering through a steam-heated funnel (Note 7), and cooling the filtrate in an ice bath. The yield of shiny white crystals, m.p. 162–163°, is 62–79 g. (30–38%) (Note 8).

2. Notes

1. The first portion of this synthesis is very similar to the preparation of **acetylacetone** by the method of Adkins and Rainey (p. 17). The procedure and (Note 1),(Note 2),(Note 3),(Note 4),(Note 5),(Note 6) and (Note 8) for that synthesis may therefore be helpful in the present preparation.
2. A more finely powdered **sodium** can be obtained if paraffin oil ("Stanolind") is used in place of **xylene** (Gilbert Ashburn, private communication).
3. **Acetone** dried over **calcium sulfate** and distilled from **phosphorus pentoxide** is satisfactory.

4. The [ethyl formate](#) is dried over [calcium sulfate](#) and distilled.
5. If the solution becomes so thick as to make stirring difficult, it is advisable to add more anhydrous [ether](#).
6. It is important that the extraction and acidification be carried out without delay. Oxidation of the intermediate product takes place readily on exposure to air and causes the solution to become dark in color.
7. If a steam-heated funnel is not used, a larger volume of [ethanol](#) should be employed to prevent crystallization during filtration.
8. The higher yield (38%) was obtained if the commercial absolute [ethanol](#) was dried by treatment with [sodium](#) and [ethyl phthalate](#).¹

3. Discussion

[Triacetylbenzene](#) has been prepared only by the condensation of [acetone](#) with [ethyl formate](#) followed by the trimerization of the intermediate [acetylacetaldehyde](#).^{2,3}

References and Notes

1. *Org. Syntheses Coll. Vol. 2*, 155 (1943).
 2. Claisen and Stylos, *Ber.*, **21**, 1145 (1888).
 3. Kaushal, Sovani, and Deshapande, *J. Indian Chem. Soc.*, **19**, 107 (1942).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

[ethanol](#) (64-17-5)

[acetic acid](#) (64-19-7)

[ether](#) (60-29-7)

[calcium sulfate](#) (7778-18-9)

[acetone](#) (67-64-1)

[Norit](#) (7782-42-5)

[sodium](#) (13966-32-0)

[xylene](#) (106-42-3)

[ethyl formate](#) (109-94-4)

[ethyl phthalate](#)

[Acetylacetone](#) (123-54-6)

[acetylacetaldehyde](#)

1,3,5-Triacetylbenzene,
Benzene, 1,3,5-triacetyl (779-90-8)

triacetylbenzene

phosphorus pentoxide (1314-56-3)