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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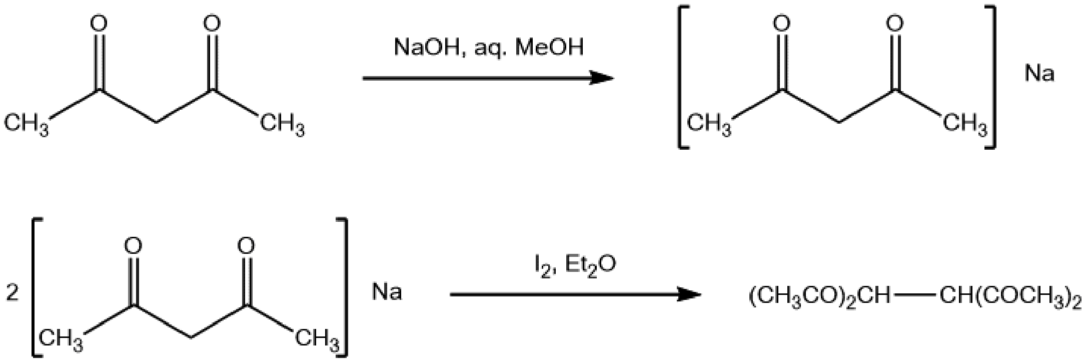
TETRAACETYLETHANE

[2,5-Hexanedione, 3,4-diacetyl-]



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1. Procedure

A. *Sodium acetylacetonate*. A solution is prepared by dissolving 40 g. (1 mole) of sodium hydroxide in 50 ml. of water and adding to this 200 ml. of methanol. This solution is added, slowly with hand stirring, to 100 g. (1 mole) of acetylacetone (2,4-pentanedione) contained in a 500-ml. Erlenmeyer flask (Note 1). The creamy-white crystalline salt separates from solution immediately. The flask is stoppered and cooled in ice (or in a refrigerator) for 2 hours or overnight. The sodium salt is collected on a Büchner funnel and washed with two small portions of cold methanol (Note 2). After the salt is air-dried, it is dried further either by allowing it to stand in a vacuum desiccator at room temperature or by heating it in a vacuum oven at 100° for 3 hours (Note 3). The anhydrous product, which is stable and can be stored indefinitely in a stoppered jar, weighs 70–80 g. (57–66%).

B. *Tetraacetylethane*. Sodium acetylacetonate is ground to a fine powder in a mortar, and 24.4 g. (0.2 mole) of the anhydrous material or 28.9 g. of the hydrate (Note 3) is weighed into a 1-l. Erlenmeyer flask. After 300 ml. of ether has been added, the suspension is stirred vigorously at room temperature with a magnetic stirrer. To the stirred mixture is added, dropwise from a separatory funnel, a solution of 25.4 g. (0.1 mole) of iodine dissolved in 300 ml. of ether. The rate of addition is maintained roughly constant by occasional adjustments of the stopcock, and the total addition is completed in about 2.5 hours. The reaction mixture is then poured into a large Erlenmeyer flask, and the ether is allowed to evaporate overnight at room temperature in a hood (Note 4). To the contents of the flask there is then added 500 ml. of water, and the mixture is allowed to stand for 2 hours. The remaining solid is collected on a Büchner funnel, washed several times with water, and finally dried in a vacuum desiccator. The yield (Note 5) of white solid, m.p. 185–188°, is 11–13 g. For purification, the product is taken up in 500–700 ml. of boiling methanol and the hot solution is filtered through a semi-fluted filter paper in a heated funnel. The filtrate is allowed to stand in the refrigerator for several hours. There is collected from the filtrate 8.0–11.7 g. (41–59%) of white crystals, m.p. 192–193° (cor.).

2. Notes

1. Eastman practical grade acetylacetone was found to be sufficiently pure for the preparation.
2. Washing with methanol decreases the yield somewhat but improves the purity of the product visibly. Additional, but less pure, sodium salt can be obtained if desired by combining the filtrate and washings, and evaporating.
3. The sodium salt dried in a vacuum oven is anhydrous, while that dried in a vacuum desiccator was found to contain 15.6% water.
4. Some hazard is always involved in the evaporation of ether to dryness. To minimize the hazard,

peroxide-free ether should be used and the evaporation conducted behind a shield. No difficulties have been encountered in the submitter's laboratory with a number of these preparations using previously unopened cans of anhydrous ether. If desired, the ether could be recovered by distillation. The explosive hazard is probably increased, however, by such a procedure.
5. The yield is essentially the same whether anhydrous or hydrated sodium acetylacetonate is used.

3. Discussion

Tetraacetylethane has been prepared previously both by the use of sodium metal[2] and of sodium hydride[3] with acetylacetone followed by addition of iodine. Also, the compound has been prepared in low yield by the reaction of diacetyl peroxide with acetylacetone[4] and by the electrolysis of acetylacetone in an alcohol-water solution.[2] The present method, although similar to those first mentioned, is somewhat more convenient and does not require anhydrous conditions.

References and Notes

1. Westinghouse Research Laboratories, Pittsburgh 35, Pennsylvania.
2. Mulliken, *Am. Chem. J.*, **15**, 523 (1893).
3. Mosby, *J. Chem. Soc.*, **1957**, 3997.
4. Kharasch, McBay, and Urry, *J. Am. Chem. Soc.*, **70**, 1269 (1948).

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

Sodium acetylacetonate

methanol (67-56-1)

ether (60-29-7)

sodium hydroxide (1310-73-2)

iodine (7553-56-2)

sodium (13966-32-0)

Acetylacetone,
2,4-pentanedione (123-54-6)

sodium hydride (7646-69-7)

Tetraacetylethane

2,5-Hexanedione, 3,4-diacetyl- (5027-32-7)

diacetyl peroxide (110-22-5)