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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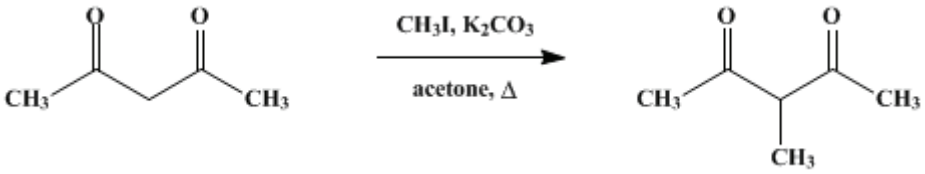
Organic Syntheses, Coll. Vol. 5, p.785 (1973); Vol. 42, p.75 (1962).

3-METHYLPENTANE-2,4-DIONE

[2,4-Pentanedione, 3-methyl-]



Submitted by A. W. Johnson, E. Markham, and R. Price[1].
Checked by Virgil Boekelheide and M. Kunstmann.

1. Procedure

A mixture of 65.2 g. (0.65 mole) of pentane-2,4-dione, 113 g. (0.80 mole) of methyl iodide, 84 g. of anhydrous potassium carbonate (Note 1), and 125 ml. of acetone is placed in a 500-ml. round-bottomed flask fitted with a reflux condenser and a calcium chloride guard tube. The mixture is heated under reflux for 20 hours and is then allowed to cool. The insoluble material is removed by filtration and washed with acetone (Note 2). The combined filtrate and acetone washings are concentrated on the steam bath (Note 3), and the residual oil is distilled. There is collected 56-57 g. (75-77%) of a colorless oil, b.p. 170–172°/760 mm.., n_D^{24} 1.4378 (Note 4).

2. Notes

1. The potassium carbonate is dried at 100° for 2 hours before use.
2. Thorough washing of the inorganic residues is essential and requires about 200 ml. of acetone.
3. During removal of the acetone, potassium iodide is deposited and it is advisable to decant the crude 3-methylpentane-2,4-dione from this material before distillation.
4. It has been reported by A. M. Roe and J. B. Harbride (private communication) that this procedure yields a product containing 20–25% of 3,3-dimethylpentane-2,4-dione as shown by gas chromatography. The amount of the dialkylation product is said to be reduced to 5–10% when the reflux period is shortened from 20 to 4.5 hours. The impurity is not readily removed, but it does not interfere with the preparation of 2,3,4,5-tetramethylpyrrole [this volume, p. 1022].
The same authors report that the work-up of the reaction may be improved by adding 250 ml. of petroleum ether (b.p. 40–60°) to the cold reaction mixture before filtering, and washing the solids with a 1:1 mixture of acetone and petroleum ether. With this change it is not necessary to decant the product from the precipitated potassium iodide as recommended in (Note 3).

3. Discussion

3-Methylpentane-2,4-dione has been prepared by the reaction of the sodium derivative of pentane-2,4-dione with methyl iodide in a sealed tube at 140°,[2] and from the sodium[3] and potassium[4] derivatives of pentane-2,4-dione and methyl iodide in alcoholic solution. It has also been prepared by the reaction of methyl iodide and pentane-2,4-dione in the presence of potassium carbonate in alcoholic or ethereal solution[5] and in acetone solution,[6,7] and by heating 2-aminopenten-4-one with methyl iodide at 100°.[8] The present modification affords improved yields.

4. Merits of Preparation

The method presented here has also been used for the preparation of 3-ethyl- and 3-isopropylpentane-2,4-diones and is probably of general applicability in the preparation of 3-alkylpentane-2,4-diones.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 1022

References and Notes

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7. A. M. Roe and J. B. Harbridge, *Chem. & Ind. (London)*, 182 (1965).
8. A. Combes and C. Combes, *Bull. Soc. Chim. France*, [3] **7**, 785 (1892).

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

petroleum ether

sodium derivative of pentane-2,4-dione

3-ethyl- and 3-isopropylpentane-2,4-diones

potassium carbonate (584-08-7)

potassium iodide (7681-11-0)

acetone (67-64-1)

sodium (13966-32-0)

potassium (7440-09-7)

Methyl iodide (74-88-4)

pentane-2,4-dione (123-54-6)

2,3,4,5-Tetramethylpyrrole (1003-90-3)

3-Methylpentane-2,4-dione,
2,4-Pentanedione, 3-methyl- (815-57-6)

3,3-dimethylpentane-2,4-dione (3142-58-3)

2-aminopenten-4-one