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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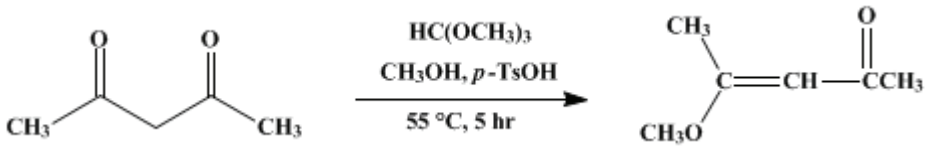
4-METHOXY-3-PENTEN-2-ONE

[3-Penten-2-one, 4-methoxy-]



Submitted by George A. Kraus, Michael E. Krolski, and James Sy[1].
Checked by Yun Gao and K. Barry Sharpless.

1. Procedure

4-Methoxy-3-penten-2-one. A flame-dried, 250-mL, one-necked flask equipped with a condenser and a drying tube is charged with 2,4-pentanedione (Note 1) (25.0 g, 250 mmol), trimethyl orthoformate (Note 2) (26.53 g, 250 mmol), *p*-toluenesulfonic acid (0.54 g. 2.8 mmol), and methanol (Note 3) (62 mL). The flask is placed in an oil bath and heated at 55°C for 5 hr. The solution is cooled and concentrated under reduced pressure. Then 50 mL of CCl_4 is added and the solution is again concentrated under reduced pressure. The crude product is distilled via a short-path condenser and collected in a flask cooled in an ice bath (Note 4). The product distills at 43–47°C (4 mm) *at an oil-bath temperature of 60°C* (Note 5). The yield of pure product is 17.3–18.8 g (61–66%) (Note 6).

2. Notes

1. 2,4-Pentanedione was obtained from Aldrich Chemical Company, Inc. Its purity was greater than 99% and was used without purification.
2. The trimethyl orthoformate used in this experiment was obtained from Aldrich Chemical Company, Inc. Its purity was listed as 98% and was used without purification.
3. Methanol was obtained from Fisher Scientific. It was anhydrous-grade methanol.
4. The checkers used a dry ice–acetone cooling bath.
5. Use of higher temperature (>65°C) results in a much lower yield.
6. The spectral properties of 4-methoxy-3-penten-1-one are as follows: IR (neat) cm^{-1}: 1674, 1590, 1165, 922. NMR ($CDCl_3$) δ: 2.15 (s, 3 H), 2.28 (s, 3 H), 3.64 (s, 3 H), 5.41 (s, 1 H).

3. Discussion

4-Methoxy-3-penten-2-one has been prepared by Awang using methanol and sulfuric acid.[2] He also determined the stereochemistry by NMR solvent shift data and observation of nuclear Overhauser effects. Our preparation is a convenient, one-pot procedure. The title compound is useful for effecting the overall γ-alkylation of enones[3] and has been used in a synthesis of prostaglandins.[4]

References and Notes

1. Department of Chemistry, Iowa State University, Ames, IA 50011.
2. Awang, D. V. C. *Can. J. Chem.* **1971**, *49*, 2672.
3. Stork, G.; Kraus, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 2351.
4. Stork, G.; Kraus, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 6747.

Appendix

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

sulfuric acid (7664-93-9)

methanol (67-56-1)

CCl_4 (56-23-5)

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

p-toluenesulfonic acid (104-15-4)

trimethyl orthoformate (149-73-5)

4-Methoxy-3-penten-2-one,
3-Penten-2-one, 4-methoxy- (2845-83-2)

4-methoxy-3-penten-1-one