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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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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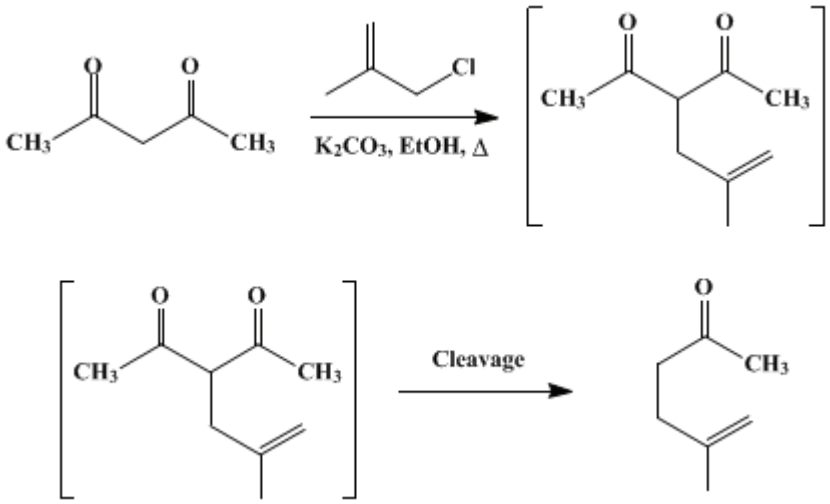
Organic Syntheses, Coll. Vol. 5, p.767 (1973); Vol. 47, p.87 (1967).

5-METHYL-5-HEXEN-2-ONE

[5-Methylene-2-hexanone]



Submitted by Sandra Boatman and Charles R. Hauser[1].
Checked by E. J. Corey and William E. Russey.

1. Procedure

In a 1-l. round-bottomed flask equipped with a condenser are placed 78.0 g. (0.56 mole) of commercial anhydrous potassium carbonate, 45.0 g. (0.50 mole) of methallyl chloride (Note 1), 55.0 g. (0.55 mole) of 2,4-pentanedione (Note 1), and 300 ml. of anhydrous ethanol (Note 2). The mixture is refluxed on a steam bath for 16 hours. The condenser is replaced by a distilling head and condenser, and about 200 ml. of ethanol is distilled from the mixture (Note 3). Ice water (600 ml.) is added to dissolve the salts, and the mixture is extracted three times with ether. The combined ether extracts are washed twice with 100 ml. of saturated sodium chloride solution, dried for 30 minutes over anhydrous magnesium sulfate, and filtered; the solvent is evaporated. The residue is distilled through a 6-in. Vigreux column using an oil bath maintained at 190° to give 26–29 g. (47–52%) of the product, b.p. 145–155° (Note 4), (Note 5).

2. Notes

1. Eastman Organic Chemicals practical grade methallyl chloride was distilled (b.p. 70–71°); Union Carbide Chemicals Co. 2,4-pentanedione was distilled (b.p. 134.5–135.5°).
2. Commercial grade absolute ethanol was dried over Linde 3A molecular sieves.
3. At this point most of the ethyl acetate, which is formed as a by-product of the reaction, also is removed.
4. The checkers used a 2-ft. spinning-band column at 200 mm. and observed b.p. 110–111.5°.
5. In the distillation residue (5.7–6.3 g.) remain other byproducts, presumably 1,1-dimethallyl-2-propanone, 3-methallyl-2,4-pentanedione, and 3,3-dimethallyl-2,4-pentanedione (indicated by vapor phase chromatography). The checkers carried out v.p.c. analyses using an 8-ft. column of 5% silicone oil XE-60 on Diatoport S at 100° for analysis of the distillate and 175° for analysis of the residue.

3. Discussion

5-Methyl-5-hexen-2-one has been prepared by alkylation of acetoacetic ester with methallyl chloride, followed by cleavage; the overall yield in the two steps was 51%.[2]

4. Merits of the Preparation

The present procedure, which is characterized by its extreme simplicity, has been employed to prepare various ketones of type RCH_2COCH_3 from 2,4-pentanedione,[3] as indicated in Table I.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 9, 275

TABLE I ALKYLATION AND CLEAVAGE OF 2,4-PENTANEDIONE

Alkyl Halide	Ketone	% Yield
Benzyl chloride	4-Phenyl-2-butanone	73
o-Bromobenzyl bromide	4-(*o*-Bromophenyl)-2-butanone	75
m-Bromobenzyl bromide	4-(*m*-Bromophenyl)-2-butanone	78
o-Chlorobenzyl chloride	4-(*o*-Chlorophenyl)-2-butanone	78
m-Chlorobenzyl bromide	4-(*m*-Chlorophenyl)-2-butanone	65
p-Chlorobenzyl bromide	4-(*p*-Chlorophenyl)-2-butanone	62
m-Fluorobenzyl chloride	4-(*m*-Fluorophenyl)-2-butanone	60
m-Nitrobenzyl chloride	4-(*m*-Nitrophenyl)-2-butanone	65
α-Chloromethylnaphthalen	4-(α-Naphthyl)-2-butanone	61
Phenacyl chloride	1-Phenyl-1,4-pentanedione	55
n-Butyl iodide	2-Heptanone	60

References and Notes

1. Department of Chemistry, Duke University, Durham, North Carolina. This work was supported by the National Science Foundation.
2. W. Kimel and A. C. Cope, *J. Am. Chem. Soc.*, **65**, 1992 (1943).
3. S. Boatman, T. M. Harris, and C. R. Hauser, *J. Org. Chem.*, **30**, 3321 (1965).

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

ethanol (64-17-5)

potassium carbonate (584-08-7)

ethyl acetate (141-78-6)

ether (60-29-7)

sodium chloride (7647-14-5)

benzyl chloride (100-44-7)

2-Heptanone (110-43-0)

magnesium sulfate (7487-88-9)

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

phenacyl chloride (532-27-4)

α-Chloromethylnaphthalen (86-52-2)

methallyl chloride (563-47-3)

o-Chlorobenzyl chloride (611-19-8)

5-Methyl-5-hexen-2-one,
5-Methylene-2-hexanone (3240-09-3)

3,3-dimethallyl-2,4-pentanedione

4-Phenyl-2-butanone (2550-26-7)

4-(α-Naphthyl)-2-butanone

1-Phenyl-1,4-pentanedione (583-05-1)

4-(p-Chlorophenyl)-2-butanone (3506-75-0)

n-Butyl iodide (542-69-8)

p-chlorobenzyl bromide (622-95-7)

o-Bromobenzyl bromide (3433-80-5)

4-(o-Bromophenyl)-2-butanone

m-Bromobenzyl bromide (823-78-9)

4-(m-Bromophenyl)-2-butanone

4-(o-Chlorophenyl)-2-butanone

m-Chlorobenzyl bromide (766-80-3)

4-(m-Chlorophenyl)-2-butanone

m-Fluorobenzyl chloride (456-42-8)

4-(m-Fluorophenyl)-2-butanone

m-Nitrobenzyl chloride (619-23-8)

4-(m-Nitrophenyl)-2-butanone

1,1-dimethallyl-2-propanone

3-methallyl-2,4-pentanedione