



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.

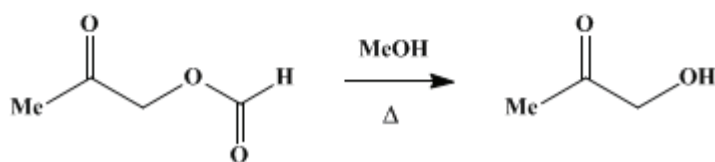
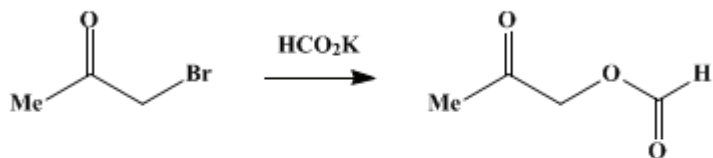
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.5 (1943); Vol. 10, p.1 (1930).

ACETOL

[2-Propanone, 1-hydroxy-]



Submitted by P. A. Levene and A. Walti.

Checked by Frank C. Whitmore and J. Pauline Hollingshead.

1. Procedure

In a 3-l. round-bottomed flask fitted with a 75-cm. Liebig condenser is placed 210 g. of **potassium hydroxide** (purified with **alcohol**) dissolved in 1.5 l. of anhydrous **methyl alcohol**. The solution is cooled to below 50° (**Note 1**), 300 g. of purified **ethyl formate** is added, and the mixture is refluxed for two hours (**Note 2**) and (**Note 3**).

Then 410 g. (251 cc., 3 moles) of **bromoacetone** (p. 88) is added, and the mixture is refluxed for sixteen hours on a water bath at 95–97°. At the end of the operation the solution is cooled to 0° in an ice-salt bath. The **potassium bromide** which settles is filtered on a cooled suction filter, and the filtrate is fractionated.

The fraction boiling at 23–35°/12 mm. is discarded, as it contains very little **acetol**. The main fraction distils at 35–47°/12 mm. and weighs 160 g. This material is refractionated, and the portion boiling at 40–43°/12 mm. is collected. The yield is 120–130 g. (54–58 per cent of the theoretical amount) (**Note 4**).

2. Notes

1. It is necessary to cool the mixture below 50° to prevent loss of the volatile **ethyl formate**.
2. Technical **ethyl formate** was purified by washing with 3 per cent **sodium carbonate** solution, then with cold water, drying over anhydrous **sodium sulfate**, filtering, and fractionating. Compare p. 180. It is very important that all the materials used in the synthesis of **acetol** be anhydrous, as otherwise condensation products are formed.
3. If commercial **potassium formate** is used it should be dried under reduced pressure at 80°. One and one-half to two moles should be used per mole of the bromo compound.
4. **Acetol** polymerizes very readily on standing but remains unchanged when dissolved in an equal volume of **methyl alcohol**.

3. Discussion

Acetol has usually been prepared by the reaction between bromoacetone and sodium or potassium formate or acetate, followed by hydrolysis of the ester with methyl alcohol.^{1, 2} Treatment of glycerol³ or propylene glycol⁴ at 200–300° with a dehydrogenating catalyst leads to the formation of acetol, while the direct oxidation of acetone with Baeyer and Villiger's acetone-peroxide reagent furnishes acetol together with pyruvic acid.⁵

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 88
- Org. Syn. Coll. Vol. 2, 545
- Org. Syn. Coll. Vol. 7, 356

References and Notes

1. Nef, Ann. **335**, 247, 260 (1904).
 2. Urion, Ann. chim. (11) **1**, 78 (1934).
 3. Holmes, Brit. pat. 428,462 [C. A. **29**, 6908 (1935)].
 4. Carbide and Carbon Chemicals Corporation, U. S. pat. 2,143,383 [C. A. **33**, 2914 (1939)].
 5. Pastureau, Bull. soc. chim. (4) **5**, 227 (1909).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

sodium or potassium formate

Baeyer and Villiger's acetone-peroxide reagent

alcohol (64-17-5)

Acetol (64-19-7)

methyl alcohol (67-56-1)

glycerol (56-81-5)

sodium carbonate (497-19-8)

sodium sulfate (7757-82-6)

acetone (67-64-1)

potassium hydroxide (1310-58-3)

potassium bromide (7758-02-3)

ethyl formate (109-94-4)

Pyruvic acid (127-17-3)

2-Propanone, 1-hydroxy- (116-09-6)

Bromoacetone (598-31-2)

potassium formate

propylene glycol (57-55-6)