



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

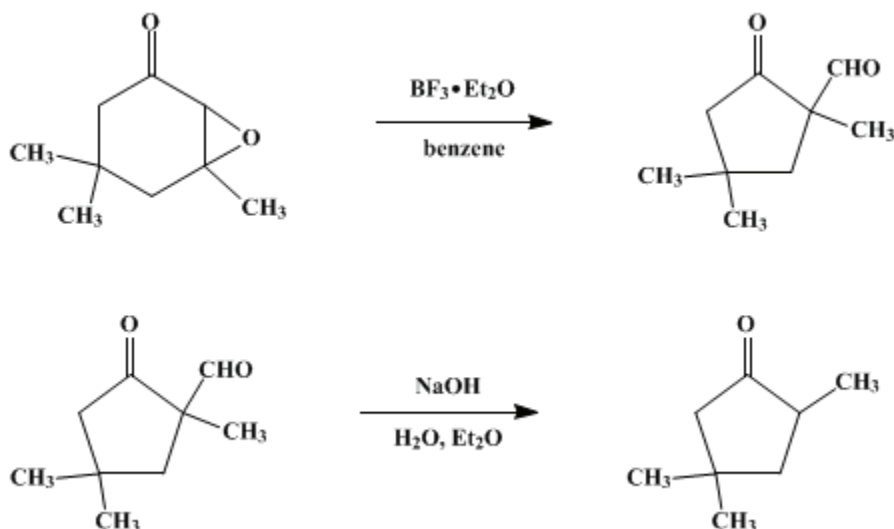
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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2,4,4-TRIMETHYLCYCLOPENTANONE**[Cyclopentanone, 2,4,4-trimethyl-]**

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Checked by James Cason and Ralph J. Fessenden.

1. Procedure

In a 1-l. separatory funnel is placed a solution of 38.6 g. (0.25 mole) of [isophorone oxide](#) ([Note 1](#)) in 400 ml. of reagent grade [benzene](#). To the solution is added 20 ml. (0.16 mole) of [boron trifluoride etherate](#) ([Note 2](#)). The resulting solution is mixed by swirling, allowed to stand for 30 minutes, then diluted with 100 ml. of [ether](#) and washed with 100 ml. of water ([Note 3](#)). The organic layer is shaken for 1–2 minutes with a solution of 40 g. (1.0 mole) of [sodium hydroxide](#) in 200 ml. of water ([Note 4](#)) and then washed with a second 100-ml. portion of water. The combined aqueous solutions are cooled briefly in running water and then extracted with two 50-ml. portions of [ether](#). The ethereal extracts are added to the [benzene-ether](#) solution ([Note 5](#)), and the combined solution, after drying over anhydrous [magnesium sulfate](#), is concentrated by distillation through a Claisen head. When the temperature of the distillate reaches about 80° ([Note 6](#)), the residual liquid is fractionally distilled ([Note 7](#)) under reduced pressure. The yield of [2,4,4-trimethylcyclopentanone](#), b.p. 61–62°/21 mm., n_D^{28} 1.4278–1.4288, is 17.7–19.8 g. (56–63%) ([Note 8](#)).

2. Notes

- The preparation of [isophorone oxide](#) is described on [p. 552](#)
- A practical grade of [boron trifluoride etherate](#), purchased from Eastman Kodak Company, was redistilled before use. The pure etherate boils at 126°.
- If the organic layer is dried over [magnesium sulfate](#) and fractionally distilled at this point, both [2,4,4-trimethylcyclopentanone](#) and [2-formyl-2,4,4-trimethylcyclopentanone](#), b.p. 49–50° (2 mm.), n_D^{25} 1.4495, may be isolated. The pot residue from this distillation contains a small amount of the enol form of [3,5,5-trimethyl-1,2-cyclohexanedione](#) which crystallizes from petroleum ether as white needles, m.p. 92–93°.
- The specified period of shaking is sufficient to ensure complete deformylation of the intermediate β -ketoaldehyde. Ordinarily, no difficulty is experienced with emulsification provided that the recommended quantity (or more) of [ether](#) is added to the reaction mixture.
- Acidification of the residual aqueous solution followed by extraction with [ether](#) permits the isolation of about 1 g. of the enol form of [3,5,5-trimethyl-1,2-cyclohexanedione](#) ([Note 3](#)).

6. At this point about 150–200 ml. of liquid remains in the still pot. If the distillation is continued, the peppermint-like odor of the product, **2,4,4-trimethylcyclopentanone**, can be detected in the distillate.

7. The submitters used a 24-cm. jacketed Vigreux column for this distillation. The checkers used a simple type of Podbielniak column, 50 cm. in length, with heated jacket and partial reflux head; after the last of the **benzene** had been distilled through the column, the following fractions were received:

Wt., g.	B.P./15 mm.	n_D^{28}
0.7	35–54°	1.4288
0.7	54–55°	1.4278
7.5	55°	1.4278
9.5	55°	1.4278
4.9	Residue, m.p. 80–90°	

Thus a rather good sample of product may be obtained without use of fractionating equipment.

8. If an appreciable quantity of higher-boiling material (consisting of **2-formyl-2,4,4-trimethylcyclopentanone**; (Note 4)) remains after the product has been collected, the residue should be dissolved in **ether** and shaken with aqueous **sodium hydroxide** as described in the procedure. After the ethereal extract has been dried over **magnesium sulfate**, distillation will permit the isolation of an additional quantity of **2,4,4-trimethylcyclopentanone**.

3. Discussion

2,4,4-Trimethylcyclopentanone has been prepared by the oxidation of **1-hydroxy-2,4,4-trimethylcyclopentanecarboxylic acid** with **lead dioxide** in **sulfuric acid**,² by the hydrogenation of **2,4,4-trimethyl-2-cyclopentenone**,^{3,4} by the Clemmensen reduction of **dimethyldihydroresorcinol**,^{5,6} by the distillation of powdered **2,4,4-trimethyladipic acid** with **sodium hydroxide**,⁷ and by the saponification and decarboxylation of **ethyl 2-keto-1,4,4-trimethylcyclopentanecarboxylate**.^{8,9} The rearrangement of **isophorone oxide**¹⁰ appears to represent the optimum combination of favorable yield and convenient procedure.

References and Notes

1. Massachusetts Institute of Technology, Cambridge, Massachusetts.
2. Wallach, *Ann.*, **414**, 296 (1918).
3. Fjader, *Suomen Kemistilehti*, **5**, Suppl. 27 (1932) [*Chem. Zentr.*, **1932 I**, 3172].
4. Nazarov and Bukhmutskaia, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, **1947**, 205 [*C. A.*, **42**, 7733 (1948)].
5. Dey and Linstead, *J. Chem. Soc.*, **1935**, 1063.
6. Auterinen, *Suomen Kemistilehti*, **10B**, 22 (1937) [*C. A.*, **32**, 509 (1938)].
7. Birch and Johnson, *J. Chem. Soc.*, **1951**, 1493.
8. Qudrati-Khuda and Mukherji, *J. Indian Chem. Soc.*, **23**, 435 (1946).
9. Chakravarti, *J. Chem. Soc.*, **1947**, 1028.
10. House and Wasson, *J. Am. Chem. Soc.*, **79**, 1488 (1957).

Appendix

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

petroleum ether

β -ketoaldehyde

sulfuric acid (7664-93-9)

Benzene (71-43-2)

ether (60-29-7)

sodium hydroxide (1310-73-2)

magnesium sulfate (7487-88-9)

dimethyldihydroresorcinol

boron trifluoride etherate (109-63-7)

Isophorone oxide (10276-21-8)

2,4,4-Trimethylcyclopentanone,
Cyclopentanone, 2,4,4-trimethyl- (4694-12-6)

2-formyl-2,4,4-trimethylcyclopentanone

3,5,5-trimethyl-1,2-cyclohexanedione

1-hydroxy-2,4,4-trimethylcyclopentanecarboxylic acid

2,4,4-trimethyl-2-cyclopentenone

2,4,4-trimethyladipic acid

ethyl 2-keto-1,4,4-trimethylcyclopentanecarboxylate

lead dioxide