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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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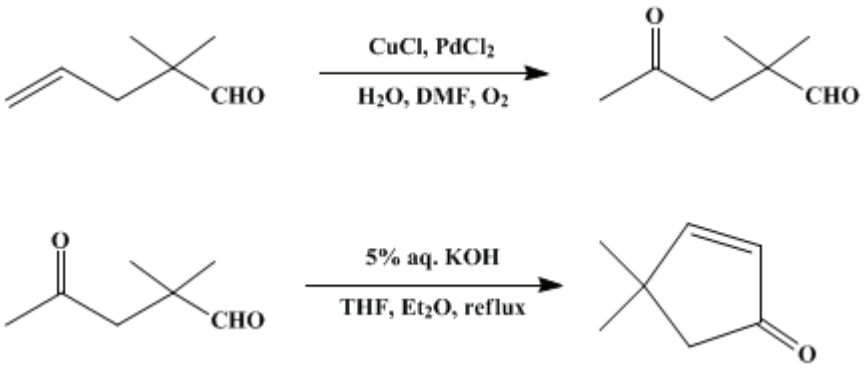
4,4-DIMETHYL-2-CYCLOPENTEN-1-ONE

[2-Cyclopenten-1-one, 4,4-dimethyl-]



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Checked by David M. Fink and Andrew S. Kende.

1. Procedure

A. *2,2-Dimethyl-4-oxopentanal.* (See (Note 1).) Oxygen is bubbled for 2 hr through a stirred solution of copper(I) chloride (32.8 g, 0.33 mol), palladium(II) chloride (1.19 g, 0.007 mol), 829 mL of dimethylformamide, and 331 mL of water in a 2-L, three-necked, round-bottomed flask cooled in a water bath. 2,2-Dimethyl-4-pentenal (185.6 g, 1.66 mol) (Note 2) is added to the solution and oxygen is bubbled through for an additional 60 hr at room temperature. The solution is acidified to litmus with 10% hydrochloric acid and extracted 4 times with 200 mL of ethyl ether. The combined organic layers are washed 3 times with 200 mL of saturated sodium chloride solution and dried over sodium sulfate. The ether is removed first by rotary evaporation and then under reduced pressure (0.2 mm). In this way 133.6 g (1.04 mol) of keto-aldehyde is obtained in 62.7% yield. The original aqueous layer is saturated with sodium chloride and extracted 5 times with 200 mL of anhydrous ethyl ether. The combined organic layers are washed 3 times with 200 mL of saturated sodium chloride solution and dried over sodium sulfate. Solvent is removed by rotary evaporation and vacuum pump. An additional 31.5 g (0.25 mol) of keto-aldehyde is recovered to give a total yield of 78% (Note 3), bp 32°C (0.3 mm) (Note 4).

B. *4,4-Dimethyl-2-cyclopenten-1-one.* A 3-L, round-bottomed flask, containing a solution of 600 mL of aqueous 5% potassium hydroxide, 300 mL of tetrahydrofuran, 1350 mL of ethyl ether, and 165.1 g (1.29 mol) 2,2-dimethyl-4-oxopentanal, is equipped with a mechanical stirrer and a reflux condenser. The solution is heated under reflux for 66 hr under a nitrogen atmosphere. On completion, the organic layer is washed 3 times with 200 mL of saturated sodium chloride solution and dried over sodium sulfate. The aqueous layer is extracted 3 times with 200 mL of anhydrous ethyl ether. The resulting organic layers are washed 3 times with saturated sodium chloride solution and dried over sodium sulfate. All organic layers are evaporated using aspirator vacuum and a rotary evaporator and combined. The residual ether is removed under reduced pressure to yield 89.7 g (63%) of 4,4-dimethyl-2-cyclopenten-1-one, bp 32°C (0.3 mm) (Note 5),(Note 6),(Note 7).

2. Notes

1. This procedure was originally described by Magnus.[2]
2. 2,2-Dimethyl-4-pentenal was prepared as described in *Org. Synth., Coll. VII* **1990**, 177.
3. The product is sufficiently pure to be used in the next reaction without purification.
4. The spectral properties of the product are as follows: IR (neat) cm^{-1}: 2990, 2730, 1740, 1485, 1380; ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.12 (s, 6 H), 2.14 (s, 3 H), 2.7 (s, 2 H), 9.52 (s, 1 H).
5. This product is volatile. The checkers found one-third of the product in a vacuum trap after 24 hr at ca. 5 mm.

6. The checkers distilled the product (Kugelrohr 8 mm, 80°C) and obtained yields of 83% (one-third scale) and 79% (two-thirds scale).
7. The spectral properties of the product are as follows: IR (neat) cm^{-1}: 2970, 2890, 1730, 1600, 1480, 1430; ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.20 (s, 6 H), 2.21 (s, 2 H), 5.97 (d, 1 H, J = 6), 7.46 (d, 1 H, J = 6).

3. Discussion

4,4-Dimethyl-2-cyclopenten-1-one is a valuable starting material in terpenoid synthesis and in cases where a *gem*-dimethylcyclopentane unit needs to be introduced. It is useful as a starting material in further functionalization. Its preparation by the method of Magnus[2] is amenable to large scale synthesis.

Acknowledgment

The authors thank Professor P. D. Magnus for permission to use his method for the scale up reported here.

References and Notes

1. Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061.
2. Magnus, P. D.; Nobbs, M. S. *Synth. Commun.* **1980**, *10*, 273.

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

hydrochloric acid (7647-01-0)

ether,
ethyl ether (60-29-7)

sodium chloride (7647-14-5)

sodium sulfate (7757-82-6)

oxygen (7782-44-7)

nitrogen (7727-37-9)

potassium hydroxide (1310-58-3)

copper(I) chloride (7758-89-6)

palladium(II) chloride (7647-10-1)

Tetrahydrofuran (109-99-9)

dimethylformamide (68-12-2)

2,2-Dimethyl-4-pentenal (5497-67-6)

4,4-Dimethyl-2-cyclopenten-1-one,
2-Cyclopenten-1-one, 4,4-dimethyl- (22748-16-9)

2,2-Dimethyl-4-oxopentanal (61031-76-3)