



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.

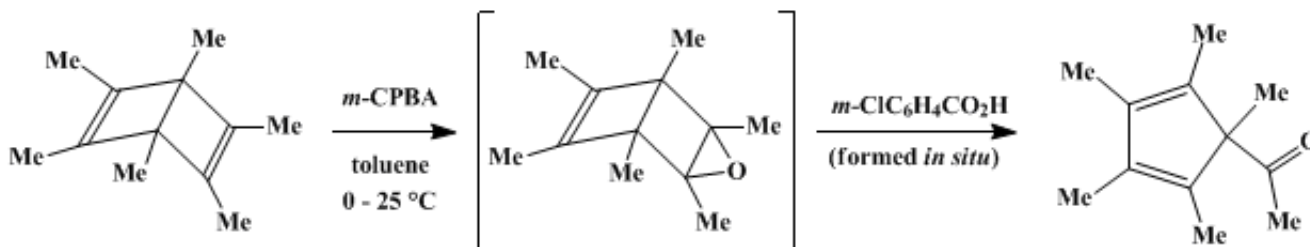
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

5-ACETYL-1,2,3,4,5-PENTAMETHYLCYCLOPENTADIENE

[Ethanone, 1-(1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)-]



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1. Procedure

*Caution! Reactions and subsequent operations involving peracids and peroxy compounds should be run behind a safety shield. Peroxy compounds should be added to the organic material, never the reverse. For relatively fast reactions, the rate of addition of the peroxy compound should be slow enough so that it reacts rapidly and no significant unreacted excess is allowed to build up. The reaction mixture should be stirred efficiently while the peroxy compound is being added, and cooling should generally be provided since many reactions of peroxy compounds are exothermic. New or unfamiliar reactions, particularly those run at elevated temperatures, should be run first on a small scale. Reaction products should never be recovered from the final reaction mixture by distillation until all residual active oxygen compounds (including unreacted peroxy compounds) have been destroyed. Decomposition of active oxygen compounds may be accomplished by the procedure described in Korach, M.; Nielsen, D. R.; Rideout, W. H. *Org. Synth.* 1962, 42, 50 (*Org. Synth.* 1973, Coll. Vol. 5, 414). [Note added January 2011].*

*Caution! Explosive mixtures often result when peracids other than *m*-chloroperbenzoic acid are used in this reaction. No such problem has ever been encountered using *m*-chloroperbenzoic acid.*

A 3-l., three-necked, round-bottomed flask is fitted with a nitrogen-inlet tube, a pressure-equalizing addition funnel, and an air-driven stirring apparatus. After the system has been thoroughly purged with nitrogen, it is charged with a solution of 100 g. (0.615 mole) of 1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexa-2,5-diene (Hexamethyldewarbenzene (Note 1)) in 200 ml. of toluene. The reaction mixture is cooled to 0° with a bath of ice water and stirred rapidly while a solution of 130 g. (0.640 mole) of 85% *m*-chloroperbenzoic acid (Note 2) in 1.5 l. of chloroform is added dropwise over 3–4 hours. Throughout the addition and for 4 hours following its completion the reaction mixture is kept at 0°, after which it is stirred at room temperature for 36 hours. The white precipitate that forms during the reaction (mainly *m*-chlorobenzoic acid) is removed by filtration through a 650-ml., sintered-glass funnel (porosity 10–15 μm), and the filter cake is washed with two 100-ml. portions of chloroform. Combination of the filtrates gives a chloroform–toluene solution, which is condensed on a rotary evaporator with the water bath at 35–40°. When all of the chloroform has been removed, the residual toluene solution is diluted with 500 ml. of pentane and refiltered. The filtrate is washed with four 200-ml. portions of 10% aqueous sodium hydroxide and two 250-ml. portions of water, dried over anhydrous magnesium sulfate, and evaporated to dryness on a rotary evaporator with the water bath at 50°. Traces of toluene are removed under high vacuum (0.02 mm.) at 25°, and the residue is distilled (Note 3). Collection of material boiling between 72° and 95° (4 mm.) gives about 50 g. of crude product, which is

further purified by dissolving it in 50 ml. of pentane and cooling the pentane solution at -78° for several hours. The resulting white crystals are collected by filtration and dried, giving 31.3–37.5 g. (29–34%) of pure 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene, m.p. 54–56° (Note 4) and (Note 5).

2. Notes

- 1,2,3,4,5,6-Hexamethylbicyclo[2.2.0]hexa-2,5-diene may be purchased from Columbia Organic Chemicals, Columbia, South Carolina, or Henley Chemical Company, New York, New York.
- m*-Chloroperbenzoic acid may be purchased from Columbia Organic Chemicals or the Aldrich Chemical Company, Inc., Milwaukee, Wisconsin.
- Distillation was performed using a 30-cm., vacuum-jacketed column wrapped with heating tape and containing a spiral of wire (Nichrome or Chromel) in the center bore. The receiver portion of the assembly contained two flasks, one to collect the material that distilled below 72° and another for the desired fraction. An air-cooled condenser was used with this apparatus, since water cooling often causes the product to solidify and clog the condenser tube.
- If the product is to be used for the preparation of metal carbonyl derivatives, further usable material may be obtained from the mother liquors. Removal of pentane on a rotary evaporator leaves a yellow–orange, viscous oil that is suitable for most preparative purposes. If an extremely pure product is required, the crystalline material can be sublimed at $35\text{--}40^{\circ}$ (0.01 mm.).
- IR (cyclohexane) cm^{-1} : 1703, 1340, 1190, 1090, 960, 760; ^1H NMR (CCl_4): δ (number of protons, multiplicity): 1.0 (s, 3H), 1.5 (s, 3H), 1.7 (s, 6H), 1.9 (s, 6H).

3. Discussion

The present preparation of 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene is more reliable and convenient than that previously available.² This compound has been used to prepare many pentamethylcyclopentadienyl metal carbonyl derivatives³ and is also a convenient source of pentamethylcyclopentadiene for use in preparing other $(\text{Me}_5\text{Cp})_m\text{ML}_n$ derivatives.^{4,5}

References and Notes

1. Department of Chemistry, University of Georgia, Athens, Georgia 30602.
2. H. N. Junker, W. Schafer, and H. Niedenbruck, *Chem. Ber.*, **100**, 2508 (1967).
3. R. B. King and A. Efraty, *J. Am. Chem. Soc.*, **94**, 3773 (1972).
4. R. B. King and M. Bisnette, *J. Organomet. Chem.*, **8**, 287 (1967).
5. U. Burger, A. Delay, and F. Mazenod, *Helv. Chim. Acta*, **57**, 2106 (1974); D. Feitler and G. M. Whitesides, *Inorg. Chem.*, **15**, 466 (1976).

Appendix

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

sodium hydroxide (1310-73-2)

chloroform (67-66-3)

nitrogen (7727-37-9)

toluene (108-88-3)

Pentane (109-66-0)

magnesium sulfate (7487-88-9)

5-Acetyl-1,2,3,4,5-pentamethylcyclopentadiene,
Ethanone, 1-(1,2,3,4,5-pentamethyl-2,4-cyclopentadien-1-yl)- (15971-76-3)

1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexa-2,5-diene,
Hexamethyldewarbenzene (7641-77-2)

pentamethylcyclopentadiene (4045-44-7)

m-Chloroperbenzoic acid (937-14-4)

m-chlorobenzoic acid (535-80-8)