



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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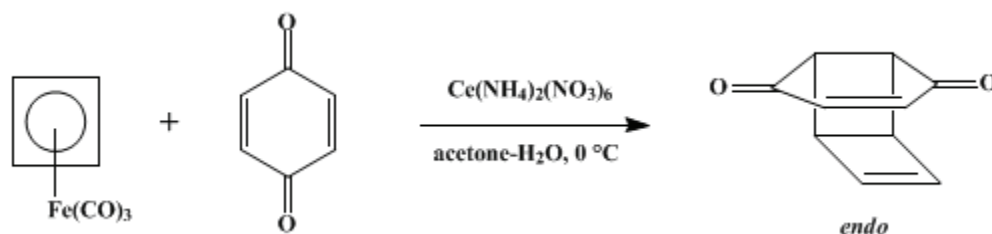
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 6, p.1002 (1988); Vol. 55, p.43 (1976).

CYCLOBUTADIENE IN SYNTHESIS: *endo*-TRICYCLO[4.4.0.0^{2,5}] DECA-3,8-DIENE-7,10-DIONE



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Checked by R. E. Ireland and G. Brown.

1. Procedure

Caution! Because of the evolution of carbon monoxide, this procedure should be carried out in a well-ventilated hood.

A 500-ml., three-necked, round-bottomed flask fitted with a sealed mechanical stirrer and an outlet leading to a gas bubbler, is charged with a solution containing 4.0 g. (0.021 mole) of cyclobutadieneiron tricarbonyl² and 2.0 g. (0.018 mole) of freshly sublimed *p*-benzoquinone (Note 1) in 72 ml. of acetone and 8 ml. of water. To the vigorously stirred, ice-cold solution, approximately 40–42 g. of ceric ammonium nitrate (Note 2) is added portionwise over a period of 10–12 minutes (Note 3), until the carbon monoxide evolution has ceased. The reaction mixture is then poured into 600 ml. of cold brine, and the resulting mixture is extracted with five 150-ml. portions of diethyl ether. The combined extracts are washed with four 250-ml. portions of water and dried over anhydrous magnesium sulfate.

Removal of the solvent under reduced pressure affords 1.9–2.1 g. of the crude yellow adduct (Note 4). This crude material is dissolved in 8 ml. of hot dibutyl ether (70–80°) and rapidly percolated through approximately 2.0 g. of Florisil (Note 5). Cooling and filtering the eluent affords 1.2–1.3 g. (40–44%) of yellow crystals, m.p. 77–80°. An additional recrystallization from dibutyl ether or ethyl acetate–hexane yields pale yellow crystals, m.p. 78.5–80° (Note 6).

2. Notes

1. In most syntheses using cyclobutadiene, it is advantageous to use an excess of the trapping agent, but here excess *p*-benzoquinone hampers isolation of the pure adduct.
2. Other oxidizing agents may be used to degrade cyclobutadieneiron tricarbonyl; in those cases in which the reactants or products are sensitive to the acidic ceric ammonium nitrate solutions, lead tetraacetate in pyridine can be used.
3. Slower addition results in a diminished yield.
4. The ¹H NMR spectrum (C₆H₆-*d*₆) indicated the presence of less than 5% *p*-benzoquinone. This material darkens upon standing, even in a refrigerator; recrystallization should be performed as soon as possible.
5. It is imperative to use a hot narrow column to prevent crystallization and to avoid passage of dark material through the column. The column was made in a Liebig condenser (6 mm. dia.). The Florisil filled 14 cm. of the condenser. A temperature of 70–80° is sufficient to melt even pure product but avoid passage of dark material.
6. The pure adduct had the following ¹H NMR spectrum (CDCl₃), δ (multiplicity, number of protons, assignment): 3.5 (broad m, 4H, cyclobutane protons), 6.20 (m, 2H, cyclobutene vinyl protons), and 6.75 (s, 2H, cyclohexene vinyl protons).

3. Discussion

This procedure is illustrative of the synthetic use of [cyclobutadieneiron tricarbonyl](#)³ as a source of highly reactive [cyclobutadiene](#). [Cyclobutadiene](#) has been employed, for example, in the synthesis of cubane, [Dewar benzenes](#), and a variety of other systems.^{3,4}

The synthesis of [endo-tricyclo\[4.4.0.0^{2,5}\]deca-3-8-dien-7,10-dione](#) and verification of its *endo*-configuration has been reported earlier.³ This adduct is a useful starting material for the syntheses of [tetracyclo\[5.3.0.0^{2,6}.0^{3,10}\]deca-4-8-diene](#),⁵ [tricyclo\[4.4.0.0^{2,5}\]deca-3,7,9-triene](#),⁶ *cis*, *syn*, *cis*-[tricyclo\[5.3.0.0^{2,6}\]deca-4-8-dien-3,10-dione](#),⁷ and [4-oxahexa-cyclo\[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}\]undecane](#).⁸

References and Notes

1. Deceased December 10, 1981; work done at Department of Chemistry, University of Texas, Austin, Texas 78712.
 2. J. Henery and R. Pettit, *Org. Synth., Coll. Vol. 6*, 422 (1988); R. Pettit and J. Henery, *Org. Synth., Coll. Vol. 6*, 310 (1988); R. H. Grubbs, *J. Am. Chem. Soc.*, **92**, 6693 (1970).
 3. J. C. Barborak, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **88**, 1328 (1966).
 4. R. Pettit, *Pure Appl. Chem.*, **17**, 253 (1968); J. C. Barborak and R. Pettit, *J. Am. Chem. Soc.*, **89**, 3080 (1967); G. D. Burt and R. Pettit, *Chem. Commun.*, 517 (1965).
 5. J. S. McKennis, L. Brener, J. S. Ward, and R. Pettit, *J. Am. Chem. Soc.*, **93**, 4957 (1971).
 6. E. Vedejs, *J. Chem. Soc. D*, 536 (1971).
 7. P. E. Eaton and S. A. Cerefice, *J. Chem. Soc. D*, 1494 (1970).
 8. J. S. Ward and R. Pettit, unpublished results.
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Appendix

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

brine

Cyclobutadieneiron tricarbonyl

[ethyl acetate](#) (141-78-6)

[diethyl ether](#) (60-29-7)

[carbon monoxide](#) (630-08-0)

[acetone](#) (67-64-1)

[pyridine](#) (110-86-1)

[dibutyl ether](#) (142-96-1)

[p-benzoquinone](#) (106-51-4)

[magnesium sulfate](#) (7487-88-9)

hexane (110-54-3)

CYCLOBUTADIENEIRON

TRICARBONYL

Dewar benzenes

ceric ammonium nitrate

CYCLOBUTADIENE

tetracyclo[5.3.0.0^{2,6}.0^{3,10}]deca-4-8-diene

tricyclo[4.4.0.0^{2,5}]deca-3,7,9-triene

4-oxahexa-cyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}.0^{8,11}]undecane

endo-Tricyclo[4.4.0.0^{2,5}]deca-3,8-diene-7,10-dione,
endo-tricyclo[4.4.0.0^{2,5}]deca-3-8-dien-7,10-dione (34231-42-0)

cis, syn, cis-tricyclo[5.3.0.0^{2,6}]deca-4-8-dien-3,10-dione

lead tetraacetate (546-67-8)