Organic Syntheses

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.

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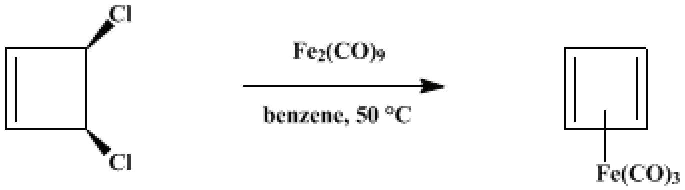
Organic Syntheses, Coll. Vol. 6, p.310 (1988); Vol. 50, p.21 (1970).

CYCLOBUTADIENEIRON TRICARBONYL

[Iron, tricarbonyl (η^4-1,3-cyclobutadiene)-]



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Checked by J. Napierski and R. Breslow.

1. Procedure

Caution! Benzene has been identified as a carcinogen; OSHA has issued emergency standards on its use. All procedures involving benzene should be carried out in a well-ventilated hood, and glove protection is required.

In a well-ventilated hood a 500-ml., three-necked flask is immersed in an oil bath and fitted with a condenser and a mechanical stirrer; a T-piece is inserted through a rubber stopper placed in the top of the condenser. One lead of the T-piece is connected to a nitrogen supply and the other to a gas bubbler. *cis*-3,4-Dichlorocyclobutene [*Org. Synth.*, **Coll. Vol. 6**, 422 (1988)], 20 g. (0.16 mole), and 125 ml. of anhydrous benzene are added to the flask, and the apparatus is flushed with nitrogen. Diiron nonacarbonyl, 25 g. (Note 1) is then added, the flow of N_2 is stopped, and the mixture is heated to 50–55°, with stirring. After about 15 minutes the initial rapid evolution of carbon monoxide becomes greatly diminished and an additional 8 g. of the nonacarbonyl is added; additional 8-g. quantities are added at intervals (approximately 15 minutes), governed by the rate of carbon monoxide evolution. The addition is continued until no more carbon monoxide is liberated (Note 2), and the reaction mixture is stirred at 50° for an additional hour. Approximately 140 g. of diiron nonacarbonyl is required for the complete conversion of the dichlorocyclobutene, the total reaction time being about 6 hours.

The contents of the flask are then filtered with suction through Filtercel and the residue, while kept in the Buchner funnel, is thoroughly washed with pentane until the washings are colorless (Note 3). The pentane and much of the benzene are evaporated from the combined filtrates with a water aspirator.

The residual liquid is transferred to a flask equipped with an efficient fractionating column and distilled under reduced pressure. Benzene is removed first, followed by considerable quantities of iron pentacarbonyl (b.p. 20°, 30 mm.); when the diiron nonacarbonyl has been removed, the pressure is reduced further and cyclobutadieneiron tricarbonyl[2] is collected as a pale yellow oil, b.p. 47° (3 mm.), yielding 13.8–14.4 g. (45–46% based on dichlorocyclobutene), (Note 4).

2. Notes

1. Diiron nonacarbonyl is readily available through photolysis of iron pentacarbonyl.[3]
2. The conversion of the dichlorocyclobutene to cyclobutadieneiron tricarbonyl can be conveniently monitored by GC. On a 5 ft. × 1/8 in. column of 20% Carbowax on Chromosorb W, under conditions where the retention time of dichlorocyclobutene is 2.6 minutes, the retention time of cyclobutadieneiron tricarbonyl is 2.4 minutes.
3. The brown insoluble residue is frequently pyrophoric if it is allowed to dry; it should be immediately wetted with water before it is disposed of.
4. In some preparations the last portion of the distillate of the complex may be dark green in color. This color is due to trace amounts of $Fe_3(CO)_{12}$. If desired, this can be readily removed by chromatography

over alumina. The submitters report a similar yield on three times the scale.

3. Discussion

Cyclobutadieneiron tricarbonyl may also be produced by the reaction of 3,4-dichlorocyclobutene with disodium irontetracarbonyl[4] and by irradiation of α-pyrone followed by treatment with diiron nonacarbonyl.[4] The method outlined here is the most convenient, especially when considerable quantities (10 g. or more) of cyclobutadieneiron tricarbonyl are required. The analogous reaction of derivatives of 3,4-dihalocyclobutenes with diiron nonacarbonyl affords the corresponding cyclobutadieneiron tricarbonyl complexes. Cyclobutadieneiron tricarbonyl can be oxidized to generate cyclobutadiene *in situ*.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 1002

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References and Notes

1. Deceased, December 10, 1981; work done at the Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712.
2. G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965).
3. E. H. Braye and W. Huebel, *Inorg. Syn.*, **8**, 178 (1966).
4. M. Rosenblum and C. Gatsonis, *J. Am. Chem. Soc.*, **89**, 5074 (1967).
5. L. Watts and R. Pettit, *Advan. Chem. Series*, "Werner Centennial," **62**, 549 (1966).
6. R. G. Amiet, P. C. Reeves, and R. Pettit, *Chem. Commun.*, 1208 (1967).

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

Cyclobutadieneiron tricarbonyl

(η^4-1,3-cyclobutadiene)-

Diiron nonacarbonyl

disodium irontetracarbonyl

Benzene (71-43-2)

carbon monoxide (630-08-0)

nitrogen (7727-37-9)

Pentane (109-66-0)

iron pentacarbonyl

α-Pyrone (504-31-4)

Iron, tricarbonyl

nonacarbonyl

dichlorocyclobutene

3,4-dichlorocyclobutene

cis-3,4-Dichlorocyclobutene (2957-95-1)