



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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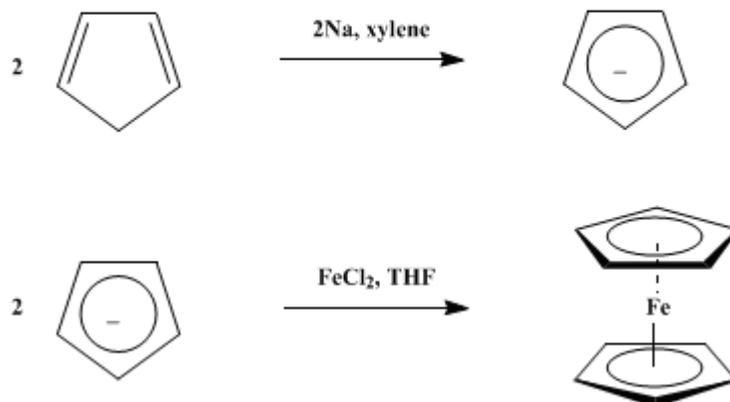
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.473 (1963); Vol. 36, p.31 (1956).

FERROCENE

[Iron, dicyclopentadienyl-]

[I. METALLIC SODIUM METHOD]



Submitted by G. Wilkinson¹

Checked by N. J. Leonard, Kenneth L. Rinehart, Jr., Donald J. Casey, and Sung Moon.

1. Procedure

In a 250-ml. three-necked flask, fitted with a mechanical stirrer, a reflux condenser, and an inlet for admission of **nitrogen**, is placed 100 ml. of **tetrahydrofuran** (Note 1). With stirring, 27.1 g. (0.166 mole) of anhydrous **ferric chloride** is added in portions, followed by 4.7 g. (0.084 g. atom) of **iron powder** (Note 2). The mixture is heated with stirring under **nitrogen** at the reflux temperature for 4.5 hours, giving a gray powder with a brown supernatant liquid.

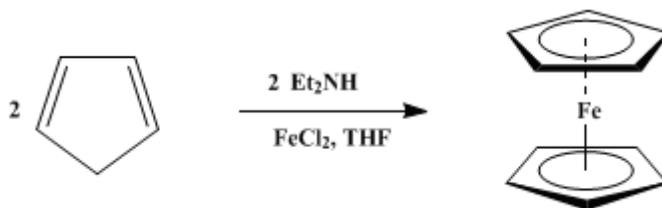
During this time, a second system is assembled, consisting of a 500-ml. three-necked flask fitted with a mechanical stirrer, a reflux condenser topped with a calcium chloride-filled drying tube attached to a xylene-filled bubbler, and a pressure-equalizing dropping funnel through which a slow stream of **nitrogen** is passed into the flask. In the flask are placed 200 ml. of sodium-dried xylene and 11.5 g. (0.5 g. atom) of **sodium**. The mixture is heated to boiling, and the **sodium** is finely dispersed by rapid stirring (Note 3). Stirring is continued while the mixture is allowed to cool in a **nitrogen** atmosphere. The cooled mixture is allowed to settle, and the bulk of the **xylene** is siphoned. **Tetrahydrofuran** (200 ml.) (Note 1) is added through the separatory funnel, and to the stirred mixture, cooled in ice, is added 42 ml. (0.5 mole) of **cyclopentadiene** (Note 4) in portions during 1 hour (Note 5). Stirring is continued for 2–3 hours in the cold, after which only a small amount of **sodium** remains unreacted.

The cooled contents of the 250-ml. flask containing **ferrous chloride** (Note 6) are added to the cold **sodium cyclopentadienide** solution while passing a stream of **nitrogen** through both flasks. The combined mixture is stirred for 1.25 hours at a temperature just below reflux. Solvent is removed by distillation, and the ferrocene is extracted from the residue with several portions of refluxing petroleum ether (b.p. 40–60°). The product is obtained by evaporation of the petroleum ether solution. Ferrocene may be purified by recrystallization from **pentane** or **cyclohexane** (**hexane**, **benzene**, and **methanol** have also been used) or by sublimation. The yield is 31–34 g. (67–73%) (Note 7), m.p. 173–174°.

2. Notes

1. Tetrahydrofuran may be purified by refluxing over solid potassium hydroxide, followed by distillation from lithium aluminum hydride. Tetrahydrofuran may be replaced by ethylene glycol dimethyl ether (dimethoxyethane). The submitter has indicated that either solvent may be freed conveniently from water, alcohols, and moderate amounts of peroxides by passing the commercial solvent through a column (2 in. diameter \times 2–3 ft. length) of Linde Air Products "Molecular Sieves" (type 13X 1/16-in. pellets), at a rate of approximately 100 ml. per minute.
2. The quality of the iron used in preparing the ferrous chloride has a marked effect on the yield of ferrocene. The checkers employed Rascher and Betzold (730 N. Franklin, Chicago, Ill.) 300-mesh iron powder, reduced by hydrogen. When 40-mesh iron filings were used, the yield of ferrocene was much lower (ca. 33%).
3. The checkers employed a "Mixmaster"-type motor and a Hershberg stirrer made from tantalum wire.
4. Cyclopentadiene, b.p. 40°, is obtained by heating commercial 85% dicyclopentadiene (e.g., from Matheson, Coleman and Bell Company, Norwood, Ohio) under a short column (3/4 in. diameter \times 8–12 in. length) filled with glass helices. The distilled cyclopentadiene is collected in a receiver which is maintained at Dry Ice temperature until the cyclopentadiene is used. Methylcyclopentadiene and other substituted cyclopentadienes such as indene may also be employed for the synthesis of the correspondingly substituted ferrocenes. In these cases, the reaction of the hydrocarbon with sodium is much slower than with cyclopentadiene, and refluxing for several hours is required to complete the reaction.
5. Under the best conditions, sodium cyclopentadienide gives pale yellow or orange solutions. Traces of air lead to red or purple solutions, as does insufficiently purified solvent, without, however, lowering the reaction yield appreciably. If 1,2-dimethoxyethane is used, in which sodium cyclopentadienide is less soluble than in tetrahydrofuran, white crystals may be obtained at this point.
6. Ferrous chloride may be substituted by ferric chloride directly, with a corresponding reduction in yield, since the sodium cyclopentadienide solution will reduce ferric chloride.
7. The submitter reported yields up to 90% by this method.

[II. DIETHYLAMINE METHOD]



Submitted by G. Wilkinson¹

Checked by N. J. Leonard, Kenneth L. Rinehart, Jr., and Peter Woo.

1. Procedure

The conditions given in the preceding preparation are used for obtaining a suspension of 0.25 mole of ferrous chloride in 100 ml. of tetrahydrofuran (Note 1), contained in a 250-ml. flask. The tetrahydrofuran is then removed under reduced pressure until the residue is almost dry. The flask is cooled in an ice bath, and to the residue is added a mixture of 42 ml. (0.5 mole) of cyclopentadiene and approximately 100 ml. (about 1 mole) of diethylamine. The mixture is stirred vigorously at room temperature for 6–8 hours or, conveniently, overnight. The excess amine is removed under reduced pressure, and the residue is extracted repeatedly with refluxing petroleum ether. The extract is filtered hot, and the solvent is evaporated to leave ferrocene. The product is purified by recrystallization from pentane or cyclohexane or by sublimation. The yield is 34–39 g. (73–84%), m.p. 173–174°.

2. Notes

1. All precautions with regard to the purification of tetrahydrofuran, the quality of the iron powder, the rapid stirring, the maintenance of a nitrogen atmosphere, and the handling of cyclopentadiene, described in the preceding preparation, are followed.

3. Discussion

The methods of preparation of ferrocene have been reviewed by Pauson² and by Fischer.³ Ferrocene has been made by the reaction of ferric chloride with cyclopentadienylmagnesium bromide,⁴ by the direct thermal reaction of cyclopentadiene with iron metal,⁵ by the direct interaction of cyclopentadiene with iron carbonyl,⁶ by the reaction of ferrous oxide and cyclopentadiene in the presence of chromic oxide,⁷ by the reaction of ferrous chloride with sodium cyclopentadienide in liquid ammonia,⁸ and from cyclopentadiene and ferrous acetylaceton-dipyridine complex.⁹ Method I is based on that developed by Wilkinson and his co-workers for ferrocene and many analogous compounds.¹⁰

Although not so generally applicable for the preparation of dicyclopentadienyl metal compounds as the sodium cyclopentadienide procedure, Method II represents the simplest preparation of ferrocene. The amine procedure also may be employed for dicyclopentadienylnickel (about 80% yield), using nickel bromide obtained by the action of bromine on nickel metal powder and 1,2-dimethoxyethane as the solvent. The method of preparation given here is a modified version^{10d} of that originally described,¹¹ and it has been studied by others.^{12,13}

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 60
- Org. Syn. Coll. Vol. 5, 434
- Org. Syn. Coll. Vol. 5, 1001
- Org. Syn. Coll. Vol. 6, 145
- Org. Syn. Coll. Vol. 6, 1037
- Org. Syn. Coll. Vol. 5, 976

References and Notes

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

petroleum ether

Ferrocene

sodium-dried xylene

ferrous acetylacetonate-dipyridine complex

ammonia (7664-41-7)

Benzene (71-43-2)

methanol (67-56-1)

hydrogen (1333-74-0)

iron,
iron filings,
iron powder (7439-89-6)

bromine (7726-95-6)

nitrogen (7727-37-9)

cyclohexane (110-82-7)

nickel metal powder (7440-02-0)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

ferric chloride (7705-08-0)

xylene (106-42-3)

diethylamine (109-89-7)

Pentane (109-66-0)

tantalum wire (7440-25-7)

indene (95-13-6)

Tetrahydrofuran (109-99-9)

lithium aluminum hydride (16853-85-3)

hexane (110-54-3)

chromic oxide (1308-38-9)

ferrous chloride (7758-94-3)

CYCLOPENTADIENE (542-92-7)

dicyclopentadiene (77-73-6)

Iron, dicyclopentadienyl-

sodium cyclopentadienide (4984-82-1)

ethylene glycol dimethyl ether,
1,2-dimethoxyethane (110-71-4)

dimethoxyethane (534-15-6)

Methylcyclopentadiene

cyclopentadienylmagnesium bromide

iron carbonyl

ferrous oxide

dicyclopentadienylnickel

nickel bromide