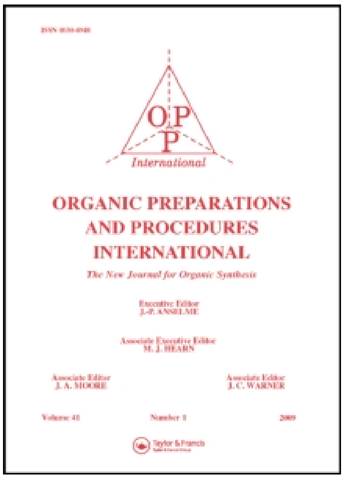

Organic Preparations and Procedures International
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

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To cite this Article Spilners, Ilgvars J. and Hartle, Robert J.(1973) 'FERROCENES FROM CYCLOPENTADIENES. 1,1'-DIMETHYLFERROCENE', Organic Preparations and Procedures International, 5: 6, 255 — 260

To link to this Article: DOI: 10.1080/00304947309356852

URL: http://dx.doi.org/10.1080/00304947309356852

ORGANIC PREPARATIONS AND PROCEDURES INT. 5(6), 255-260 (1973)

FERROCENES FROM CYCLOPENTADIENES. 1,1'-DIMETHYLFERROCENE

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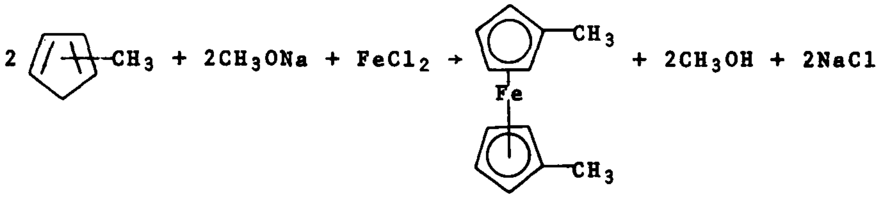
Methods of preparation of ferrocene and alkylferrocenes have been reviewed by Rosenblum.[1] Of these, the methods which are directly applicable to the preparation of both ferrocene and dimethylferrocene involve the reaction of the sodium salt of a cyclopentadiene with ferrous chloride in any of a variety of solvents including ether,[2] tetrahydrofuran,[3,4] ethylene glycol dimethyl ether,[3,5] ammonia,[6] ethanol[7] and methanol.[8] The cyclopentadienide has been formed by reaction of cyclopentadiene with sodium metal,[3,9] sodium acetylide,[10] alkoxide[3,8,11] or hydride.[3] Ferrous chloride has generally been prepared by the reduction of ferric chloride with iron powder.[4] Reported yields for these methods vary widely but for 1,1'-dimethylferrocene, they do not exceed the 70-85% range and in most cases some purification and drying of relatively expensive solvents is required.

$$2FeCl_3 + C_6H_5Cl \rightarrow 2FeCl_2 + C_6H_4Cl_2 + HCl$$



The present method[12] offers the advantages of improved yields (80-96%), the use of an inexpensive solvent which requires no pretreatment and a source of pure, dry ferrous chloride. The reaction may be described by the following equations.

$$FeCl_2 + 2NaOCH_3 \rightarrow Fe(OCH_3)_2 + 2NaCl$$

$$RC_5H_5 + NaOCH_3 \rightarrow RC_5H_4Na + CH_3OH$$

$$2RC_5H_4Na + Fe(OCH_3)_2 \rightarrow (RC_5H_4)_2\ Fe + 2NaOCH_3$$

$$R = H \text{ or alkyl}$$

The method of the preparation of ferrous chloride[13] used here gives a practically quantitative conversion from ferric chloride. An essential point is the use of excess of saturated sodium methoxide solution in methanol. External heating is required to achieve saturation of over 30% of sodium methoxide in methanol. Addition of ferrous chloride in a powdered form to the saturated solution of sodium methoxide obviates any need of additional solvent-diluent. The reaction is believed to involve ferrous methoxide as an intermediate but the significance of its actual role has not been established.

Another feature of the process is the addition of a catalytic amount of iron powder to retard dimerization of methylcyclopentadiene when it is added to the reaction mixture. Formation of dimers and oligomers in the reaction mixture would not only remove methylcyclopentadiene as a reactant but would also complicate the purification of the product. Dimerization of a methylcyclopentadiene is minimized also by adding it to the reaction mixture dropwise, thus keeping its concentration in the reaction mixture at a very low level.

Acidification of the mixture at the end of the reaction is necessary to bring the product out of the basic methanol solution and into the petroleum ether. Such acid treatment, however, oxidizes some of the 1,1'-dimethylferrocene to its water-soluble ferricinium salt. To recover this as 1,1'-dimethylferrocene, the aqueous acid layer is treated with a reducing agent, such as sodium thiosulfate or stannous chloride.

EXPERIMENTAL

Anhydrous ferric chloride was a purified sublimed grade. Sodium metal and electrolytic iron powder were of Certified Reagent grade. Chlorobenzene, methanol and all solvents were also of Certified Reagent grade and were used without further purification. Methylcyclopentadiene was freshly prepared by cracking the dimer (K & K Laboratories, Inc.) in the presence of a little iron powder above 180° and distilling the monomer as it is formed. The product was redistilled, b.p. 72°, and collected and stored in a receiver cooled in Dry Ice-Acetone.

Anhydrous Ferrous Chloride. This compound was prepared following the procedure of Kovacic and Brace.[13] Reduction of 520 g (3.2 moles) of ferric chloride was carried out in 1000 g of chlorobenzene, serving as both solvent and reducing agent, by refluxing for 3.5 hrs. Chlorobenzene is converted to dichlorobenzene in this reaction. Ferrous chloride was collected on a fritted glass funnel and washed with anhydrous benzene (dried over sodium). The freshly prepared product was used immediately.

1,1'-Dimethylferrocene. A dry, 5000-ml, three-necked flask was fitted with a reflux condenser, mechanical stirrer, thermometer, drying tube and inlet to maintain a nitrogen atmosphere throughout the reaction. The flask was charged with 2500 ml of methanol to which was added 305 g (13.3 g atoms) of freshly cut sodium in small pieces at a rate sufficient to maintain a moderate reflux. The mixture was stirred continuously and towards the end of the addition heat was applied until all the sodium had reacted.

The temperature of the sodium methoxide slurry was adjusted to 40-50° and 395 g (3.1 moles) of anhydrous ferrous chloride was added portionwise (over a period of 0.5 hrs.) followed by the addition of 1 g of iron powder. The mixture was stirred for 30 min. during which time a slight increase in temperature was observed.

Freshly distilled methylcyclopentadiene was withdrawn in 50 ml portions from its cold storage and added dropwise from an addition funnel to the brown reaction mixture at about 60°. After the addition of 468 g (5.85 moles) of methylcyclopentadiene, stirring was continued for 5 hrs. at about 55° and finally for 10 hrs. at room temperature.

The reaction mixture was poured into a suitable number of separatory funnels containing a total of 6800 ml of 12% sulfuric acid and 3000 ml of low boiling petroleum ether. After shaking, the blue aqueous layer was separated and treated with aqueous 5% sodium thiosulfate until colorless. It was then extracted with petroleum ether. The petroleum ether fractions were combined, washed repeatedly with water until neutral and dried over Drierite. After filtration, the petroleum ether was removed on a rotary evaporator and the residue dried at 80° (2 mm). The brown-orange residue weighed 600 g and melted at 38°. This represents a yield of 96% of 1,1'-dimethylferrocene based on methylcyclopentadiene charged.

This procedure was repeated several times, giving product yields ranging from 80 to 96% and melting points of 36 to 38° which agrees with reported values.[14] The product was identified and analyzed for purity by elemental analysis, glc (silicone SE 30 of OV-17 columns), mass spectrometry (7 and 70 ev) and infrared spectroscopy. The mass spectrum shows a strong parent peak at m/e 214 and other significant peaks at m/e 200, 199, 135, 134, 121, 81, 79, 77 and 56. The infrared spectrum (Nujol) has bands at 3100, 3000, 1470, 1375, 1225, 1040, 1025, 925, 850, 820 and 805 cm^{-1}.

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(Received July 27, 1973; in revised form August 31, 1973)