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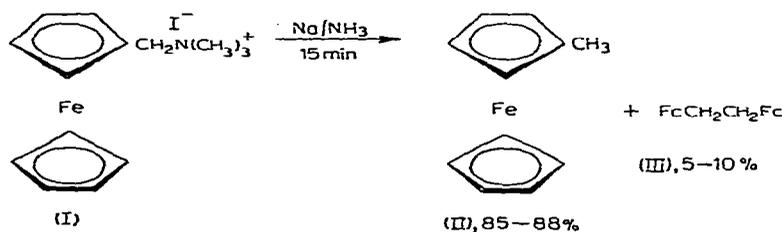
REDUCTION OF FERROCENE METHIODIDES WITH SODIUM IN LIQUID AMMONIA; A ROUTE TO ALKYLFERROCENES

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Reductive cleavage of ferrocene has been accomplished by lithium in ethylamine¹ and by catalytic hydrogenation using Raney nickel². Recently, Watt and Baye³ have reported the reduction of ferrocene with potassium/ammonia to metallic iron and $K^+C_5H_5^-$. We now wish to report that trimethyl(ferrocenylmethyl)ammonium iodide (I) under these same conditions was reduced by sodium or potassium in liquid ammonia to methylferrocene (II) in good yield with little or no evidence of the reduction of the ferrocene ring system. A small amount of a dimerization product, 1,2-diferrocenylethane (III), was also produced⁴. These results, as depicted below and summarized in Table 1, represent a new, convenient procedure for the preparation of methylferrocene*.



Methiodide (I) was suspended in liquid ammonia and treated with excess sodium metal. The best yields (85–88%) were obtained with a 6- to 12-fold excess of sodium to (I) (Table 1), although the yields were not always reproducible. After about 15 min, the reaction mixture was acidified with NH_4Cl , the methylferrocene extracted and chromatographed on alumina. The m.p. of the product (33–35°) and its IR spectrum agreed in all respects with those reported by other authors. A by-product was also isolated in yields of from 5 to 10% and was identified by its m.p. (183–187°), its IR and its NMR spectrum as the dimerization product, 1,2-diferrocenylethane (III)⁴.

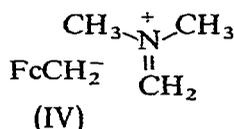
* Methylferrocene has previously been prepared by Clemmensen reduction of the aldehyde⁵, lithium aluminum hydride reduction of methyl ferrocenoate and Emde reduction of (I)⁶.

TABLE I

REDUCTION OF TRIMETHYL(FERROCENYLMETHYL)AMMONIUM IODIDE (I) WITH ALKALI METAL/AMMONIA

Molar ratio metal/methiodide (I) ^a	Alkali metal	Conditions ^b	Yield of methylferrocene (II) (%)
3:1	K		47
4:1	K	90 min reaction	54
5:1	Na	Slow addition of Na	54
7:1	Na	Large scale	88
8:1	Na		40, 58, 70
12:1	Na		85
Large excess	Na	<i>p</i> -Toluenesulfonate salt	77
Large excess	Na	5% ethanol, slow addition	45

^a All reductions were run on 10 mmoles of methiodide in 250 ml NH₃. ^b Ammonia was taken directly from a tank, the methiodide added and then the alkali metal, as described. Unless otherwise noted, the reaction was quenched after 15 min.



These results now enable us to demonstrate that the hydrocarbon impurity resulting from the Stevens rearrangement of methiodide (I) and tentatively identified as 1,2-diferrocenylethylene** is in fact methylferrocene (superimposable IR and NMR spectra). Possibly methylferrocene is produced under these conditions by some residual solvated electrons in the "converted" sodium amide or by protonation of an ion pair such as (IV) which has been suggested as an intermediate in the Stevens rearrangement⁹.

This procedure has proven applicable to substituted ferrocene methiodides. Carbinol methiodide (V) was reduced to 2-methyl(diphenylhydroxymethyl)ferrocene (VI) in 56% yield. This product was identified by its m.p. (167–168.5°) and its IR spectrum¹⁰. Likewise, dicarbinol methiodide (VII) was reduced to 2,1'-bis(diphenylhydroxymethyl)methylferrocene (VIII). It has also been shown that this procedure need not be limited to methiodides attached to an α -carbon of a ferrocene system, although the yields are not as good. Reduction of trimethyl(2-ferrocenylethyl)ammonium iodide (IX) brought a 22% yield of ethylferrocene identified by its IR spectrum¹². Not all reduction attempts of substituted ferrocene methiodides were successful; reduction of both the methiodides of 2-chloro[(dimethylamino)methyl]ferrocene¹³ and of 2-(diphenylhydroxymethyl)[2-(dimethylamino)ethyl]ferrocene¹⁴ gave only unidentifiable products.

A possible mechanism for this reduction procedure would involve attack on the quaternary nitrogen group by a solvated electron with simultaneous elimination of a ferrocenylmethyl radical, which has been proposed as an intermediate in another reduction scheme⁴. This radical could then either abstract a hydrogen atom from solvent to give methylferrocene or dimerize to give (III).

** See ref. 7; interestingly, a recent text has cited this assignment in error⁸.

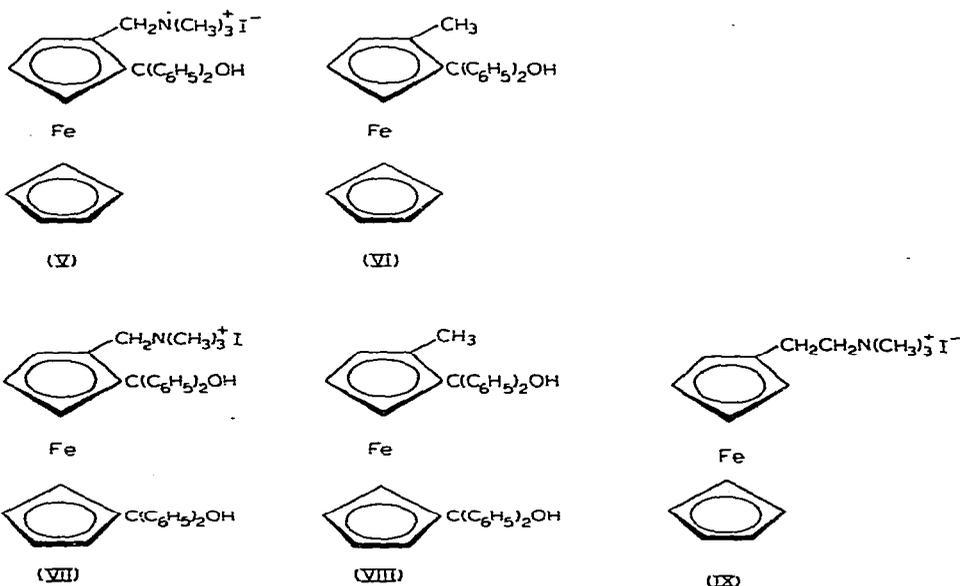
These results indicate a lack of reductive cleavage of the ring-metal bond of some substituted ferrocenes, although such a phenomenon would not have been expected from the report of Watt and Baye³. Apparently, methylferrocene is more stable to reductive cleavage than is ferrocene itself, perhaps because of destabilization of the cyclopentadienide anion by the electron donating methyl group. Initial attempts to determine the relative stabilities of ferrocene and methylferrocene in sodium/liquid ammonia over varying time periods indicate that methylferrocene is much more stable in this system than is ferrocene.

EXPERIMENTAL

Elemental analyses were performed by Alfred Bernhardt, West Germany. Melting points were determined on a Hoover melting point apparatus and were corrected. The NMR spectra were run on a Varian A-56/60 spectrometer using TMS as an internal standard. All IR spectra were determined as Nujol mulls or smears on a Perkin-Elmer Model 137 Infracord spectrometer.

Reduction of trimethyl(ferrocenylmethyl)ammonium iodide (I)

Methiodide (I) (3.85 g, 10 mmoles) was covered with about 250 ml of ammonia and the resulting mixture was stirred magnetically. Sodium beads (2.76 g, 120 mmoles) were then added as fast as possible and the mixture stirred for about 15 min. Excess ammonium chloride was then added followed by water. The ether extract of this mixture was stripped and chromatographed on alumina I. The main band was eluted with petroleum ether and was shown to be methylferrocene (II) (1.70 g, 85%), m.p. 33–34°, which was identified by its IR spectrum, its PMR spectrum and its m.p. A minor band



was eluted with 25% benzene in petroleum ether, and was shown to be 1,2-diferrocenylethane (III) (5–10% yield). It was identified by its IR spectrum, PMR spectrum, and its m.p. (183–188°)⁴.

Reduction of trimethyl{[2-(diphenylhydroxymethyl)ferrocenyl]methyl}ammonium iodide (V)

Methiodide (V) (5.9 g, 10.4 mmoles) was covered with ammonia. Sodium beads (2.5 g, 0.1 mole) were added, and the mixture stirred 15 min before quenching with ammonium chloride. Water was added and the mixture was extracted with ether. The ether layer was chromatographed on alumina I yielding a main band eluting with 50% benzene in petroleum ether. Upon evaporation, a yellow crystalline solid was obtained (m.p. 167–168.5°), which was identified as 2-methyl(diphenylhydroxymethyl)ferrocene (VI) (2.2 g, 56%) by its PMR spectra, and by comparison of its IR spectrum and m.p. to published data¹⁰.

Reduction of trimethyl(2-ferrocenylethyl)ammonium iodide (IX)

Methiodide (IX) (2.0 g, 5 mmoles) was covered with ammonia, sodium was added, and the mixture was stirred for 15–20 min after quenching with ammonium chloride, water and ether were added. The organic layer was stripped of solvent and chromatographed on alumina I yielding ethylferrocene (0.225 g, 22%) which was identified by its IR spectrum¹².

Reduction of trimethyl{[2,1'-bis(diphenylhydroxymethyl)ferrocenyl]methyl}ammonium iodide (VII)

Methiodide (VII) (5.64 g, 7.5 mmoles) was placed in a 500 ml flask and covered with 300 ml of ammonia. Sodium beads (1.77 g, 77 mmoles) were then added. The blue solution was stirred for about 5 min after the addition of the sodium was complete and then the reaction was quenched with ammonium chloride. Water was added and the mixture was extracted with ether. The organic portion was chromatographed on alumina I, yielding 2,1'-bis(diphenylhydroxymethyl)methylferrocene (VII) (3.9 g, 90%). This product melted at 107–109° but showed excessive integration in the aromatic region of its NMR spectrum. Upon repeated recrystallization from ether/hexane, rechromatography and finally drying at 78° for 4 days at ≈ 1 mm Hg, the material melted at 149–150.5°. PMR spectrum (CDCl₃); τ 8.4 (3 protons, CH₃), τ 7.0 (1 proton, OH), τ 6.5 (1 proton, OH). IR spectrum; 3.0 μ (OH), no 9, 10 μ bands¹¹. (Found: C, 78.14; H, 5.91; Fe, 9.96; O, 5.91. C₃₇H₃₂FeO₂ calcd.: C, 78.75; H, 5.72; Fe, 9.89; O, 5.67%.)

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