the addition of 1 equiv of tetra-*n*-butylammonium chloride and the precipitation of the potassium chloride before injecting the alkylating agent. The experiment involving tetraglyme was carried out by the addition of 1 equiv of tetraglyme purified by distillation from calcium hydride.

Materials.—The solvent can be readily recovered from the alkylation mixtures in about 80% yield as follows. The water is removed by flask evaporation for about 8 hr at 35–40°; the remaining liquid is dried overnight over magnesium sulfate and finally vacuum distilled from calcium hydride at 76–80° (1 mm), $n^{25}\mathrm{D}$ 1.4570 (lit.[24] 1.4570). *p*-Trifluoromethylbenzoyl chloride was converted into the ethyl ester by the procedure of Hass and Bender.[25] The product was reduced to the benzyl alcohol[25] by the method of Nystrom and Brown.[26] The alcohol was then converted[27] into the chloride.[28] *p*-Methoxybenzyl chloride[29] was prepared similarly. 2,6-Dimethylbenzyl chloride was prepared from the corresponding benzoic acid as reported by Raaen and Eastham.[30] The physical constants of these compounds agreed in all cases closely with those reported by the authors quoted.

Registry No.—Ethyl acetoacetate, 141-97-9.

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Reduction of Ferrocene Methiodides. Synthesis of the Dimethylferrocenes

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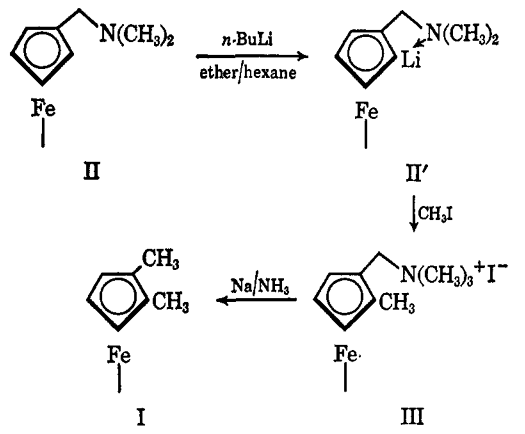
We have recently described a method which is suitable for the preparation of alkylferrocenes.[2] Utilizing this method, as well as another reduction procedure, we have succeeded in an unequivocal synthesis of 1,2-dimethylferrocene (I). This method constitutes the first direct preparation of 1,2-dimethylferrocene. Syntheses of this compound from 1,2-disubstituted precursors have been reported recently.[3]

Dimethylaminomethylferrocene (II) was lithiated with *n*-butyllithium yielding the 2-lithio intermediate II′.[4] Treatment of this intermediate with a large excess of methyl iodide and reprecipitation of the crude product from methanol/ether yielded 2-methyl-N,N,N,-N-trimethylferrocenylmethylammonium iodide (III). The crude methiodide was taken directly to the reduction step as described for methylferrocene.[2] Work-up and chromatography on neutral alumina brought a 78% yield of 1,2-dimethylferrocene. Scheme I outlines this procedure.

SCHEME I



The purity of the 1,2-dimethylferrocene was monitored by vapor phase chromatography (vpc) on a 6-ft Apiezon L (15%) on Chromosorb P column. Repeated chromatograms demonstrated conclusively that material of from 98 to 99% purity could be obtained by this method. The major impurities were methylferrocene (identical retention time as that of an authentic sample) and an unidentified material which had a longer retention time than I. Methylferrocene was probably formed by reduction of the methiodide of unmethylated amine.

Attempts to improve the purity of I by column chromatography on alumina or by recrystallization proved discouraging. However, several fractional reprecipitations of the crude methiodide from methanol/ether gave methiodide which decomposed between 178 and 179° to a black powder. An nmr spectrum of methiodide III in $CDCl_3$ exhibited a two-proton singlet at 4.78 ppm assigned to the methylene protons, a one-proton signal at 4.55 ppm assigned to the ring proton adjacent to the trimethylaminomethyl substituent, a seven-proton signal at 4.23 ppm assigned to the remaining ring protons, and a nine- and a three-proton signal at 3.23 and 2.17 ppm, respectively, assigned to the nitrogen and ring methyl groups. This purified methiodide (III) upon reduction and work-up yielded 1,2-dimethylferrocene of purity greater than 99% by vpc. 1,2-Dimethylferrocene has the following properties: parent peak at m/e 214; bp 67–68° (0.5 mm); mp 33–35°. An nmr spectrum in $CDCl_3$ showed six protons at 1.91 ppm and eight protons at 3.98 ppm. An infrared (ir) spectrum exhibited bands at 9.04 and 9.98 μ.[5]

A somewhat different route was also found to produce 1,2-dimethylferrocene. Lithiation of dimethylaminomethylferrocene and treatment with methyl iodide was effected essentially as recorded above. The methiodide thus formed was isolated and purified. Reduction of this purified methiodide by an overnight treatment with lithium aluminum hydride in tetrahydrofuran (THF) gave I in 56% yield.

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The sodium in ammonia reduction technique was also utilized for the preparation of 1,1′-dimethylferrocene. The dimethiodide of 1,1′-bis(dimethylaminomethyl)ferrocene[6] was subjected to sodium/ammonia for 15 min. The ammonia was allowed to evaporate; the crude oil after extraction was taken up in petroleum ether and chromatographed on alumina. 1,1′-Dimethylferrocene, identical in all respects with previously reported preparations,[7] was isolated in 66% yield.

In an attempt to prepare 1,3-dimethylferrocene, dimethylaminomethylation of methylferrocene was effected according to Nesmeyanov, *et al.*;[8] the resulting oil was converted into crude methiodide and reduced with sodium/ammonia in 84% yield to what had been tentatively reported as 1,3-dimethylferrocene.[8] Spectral examination revealed, however, that the reduction product, as well as the original amine, was a mixture of all three possible isomers. Others, in the instance of the amine mixture, have reported similar observations.[9]

Experimental Section[10]

Preparation of 1,2-Dimethylferrocene (I).—Dimethylaminomethylferrocene (II, 17.0 g, 0.07 mol) was placed in a 500-ml three-neck flask equipped with a nitrogen inlet and an addition funnel. *n*-Butyllithium (95 ml of a 15 *M* solution in hexane) was added over a 15-min period. The reaction was stirred for a 2.25-hr period after which time 25 g (0.17 mol) of methyl iodide was added. Soon after the addition of the methyl iodide crystallization occurred. The crude crystals were filtered and washed with ether. The solid was dissolved in chloroform, the remainder being removed by filtration. The solution was partially evaporated and petroleum ether was added to precipitate the methiodide. The solid was filtered and dried to give 20.0 g (72% yield) of 2-methyldimethylaminomethylferrocenemethiodide (III). This material was dissolved in methanol and ether was slowly added causing reprecipitation of about half of the material. The product was filtered and dried: mp 178–179° dec. *Anal.* Calcd for $C_{15}H_{22}NIFe$: C, 45.14; H, 5.57; N, 3.51; I, 31.80; Fe, 13.99. Found: C, 44.96; H, 5.46; N, 3.70; I, 32.02; Fe, 13.82.

The methiodide (III, 2.83 g, 7.5 mmol) was placed in a flask equipped with a stirrer and covered with about 200 ml of ammonia. Sodium beads (1.81 g, 79 g-atoms) were added after being cleaned with ethanol. The reaction mixture was stirred for 10 min before quenching with ammonium chloride. The evaporated mixture was partitioned between petroleum ether and water. The organic portion was chromatographed on alumina I with petroleum ether as eluent yielding 1,2-dimethylferrocene (I): mp 33–35°; 1.31 g, 89% yield (99.1% pure by vpc analysis). Anal. Calcd for $C_{12}H_{14}Fe$: C, 67.29; H, 6.54; Fe, 26.17. Found: C, 67.27; H, 6.43; Fe, 25.94. Principal ir absorptions were noted at 3.29, 3.48, 5.6–6.3 (broad), 6.80, 7.10, 7.23, 7.90, 8.30, 9.03, 9.64, 9.97, and 12.40 (broad) μ. An nmr spectrum exhibited singlets at 3.98 ppm (eight protons) and 1.91 ppm (six protons) assigned to the ring and methyl protons, respectively. A mass spectrum was run on a Consolidated Electrodynamics 21–104 (70-eV ionizing voltage, 250° inlet temperature) with the observation of significant peaks at *m/e* 214 (parent peak), 148, 121, 91, and 56.

Vapor phase chromatography of dimethylferrocene on a 15% Apiezon L on Chromosorb P, 0.25 in. × 6 ft column at 210° with a 60–100-cc He/min flow rate gave the following retention times: 8.5 min, methylferrocene, and 10 min, dimethylferrocene. On a diisodecyl phthalate on 45–60 W A/W DMCS 700 0.25 × 4 ft column at 190° with a 30-cc He/min flow rate the following retention times were recorded: 10.5 min, methylferrocene, and 14 min, 1,2-dimethylferrocene. All chromatograms were run on an F & M Laboratory chromatograph model 700.

As noted in the discussion above, 1,2-dimethylferrocene of somewhat lower purity could be obtained by taking the crude methiodide directly to the reduction step.

1,2-Dimethylferrocene was also prepared by reducing the above-produced methiodide (III, 4.0 g, 10.0 mmol) with lithium aluminum hydride (2.5 g, 0.066 mol) in 60 ml of tetrahydrofuran with overnight refluxing. A work-up procedure similar to that recorded above was employed. 1,2-Dimethylferrocene (1.2 g, 56% yield) was again isolated, this material being identical with the previously produced product as shown by the identity of their respective ir spectra.

Preparation of 1,1′-Dimethylferrocene.—The dimethiodide[11] of 1,1′-bis(dimethylaminomethyl)ferrocene (2.9 g, 4.9 mmol) was placed in a flask equipped with a stirrer and covered with ammonia. Excess (about 10:1) sodium was added, and the blue solution was stirred for 5 min before quenching with ammonium chloride. Water was added and the mixture was extracted with ether. Chromatography of the organic portion on alumina (activity I) gave, as the main band, 1,1′-dimethylferrocene (0.7 g, 66% yield), which was identified by its ir spectrum.[12]

Registry No.—I, 12126-15-7; III, 12111-93-2.

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Formation of 2-Ferrocenylbenzofuran and Some Acetylenic Derivatives of Ruthenocene[1,2]

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Several recent publications have described a variety of excellent routes for the formation of ferrocenylacetylenes.[3–5] During the course of our studies on metallocenylacetylenes, it was of interest to determine if these same methods could be employed for the

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