Anal. Calcd. for $C_8H_{18}INO_3$: C, 31.71; H, 5.98; I, 41.88; N, 4.62. Found: C, 31.64; H, 5.85; I, 41.6; N, 4.51.

2-Dimethylaminoethyl L(+)-*lactate* (V). Yield 66%; $n_D^{23.5}$ 1.4484; $[\alpha]_D^{23.5}$ −5.86° (c = 4.27, in CH_3OH); the infrared spectrum was identical with those of I and III.

L(+)-*Lactoylcholine iodide* (VI). Yield 83%; colorless plates from isopropyl alcohol–ethyl acetate melting at 90.4–91.0°; $[\alpha]_D^{23}$ −5.66° (c = 11.90, in CH_3OH); the infrared absorption spectrum was identical with that of IV.

Anal. Calcd. for $C_8H_{18}INO_3$: C, 31.71; H, 5.98; I, 41.88; N, 4.62. Found: C, 31.77; H, 5.78; I, 42.0; N, 4.43.

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The Benzal Derivative of Ferrocenylacetonitrile[1]

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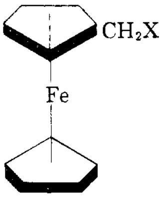
Received June 9, 1958

It has previously been shown in this laboratory that ferrocene can be aminomethylated readily to form dimethylaminomethylferrocene (I),[2] and that the methiodide of this tertiary amine (II) is a useful intermediate for the synthesis of a number of monosubstituted ferrocene derivatives.[2–6] For example, II undergoes the S_N2 displacement reaction with aqueous sodium hydroxide and potassium cyanide to give excellent yields of alcohol III[2] and nitrile IV,[5,6] respectively.

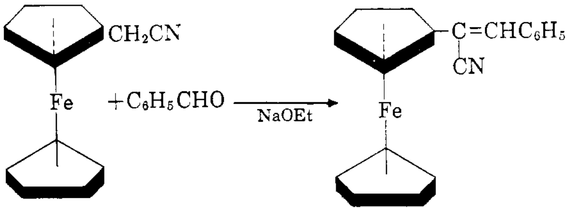


I, [X = $N(CH_3)_2$]
II, [X = $\overset{+}{N}(CH_3)_3$]
III, (X = OH)
IV, (X = CN)

Since the S_N2' type of displacement was possible,[7] definite proof for structures III and IV was desirable. This was readily accomplished with the alcohol III which produced the corresponding aldehyde on oxidation,[2] but the structure of nitrile IV was more difficult to establish with certainty.[7] The nitrile gave on hydrolysis an acid, the infrared absorption spectrum of which was identical with that of ferrocenylacetic acid prepared from acetylferrocene by the Willgerodt rearrangement.[6,8] However, the yields of this acid from the latter reaction have been low (10–20%),[8–10] and the melting points have varied somewhat, 161°,[8] 150–152°,[9] and 135–140°.[10]

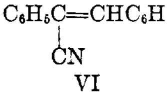
Confirmation[5] for the two-carbon side chain of structure IV was obtained by reducing the nitrile to the corresponding primary amine, which was exhaustively methylated. The resulting quaternary ammonium ion underwent β-elimination with potassium amide to form vinylferrocene.[5]

Still further evidence for structure IV has now been obtained by showing the presence of the two methylenic hydrogen atoms in the nitrile. Thus, like phenylacetonitrile,[11] ferrocenylacetonitrile IV underwent with benzaldehyde in the presence of alkali an aldol type condensation accompanied by the elimination of water to form the benzal derivative V in 80% yield.



IV V

The product exhibited an infrared absorption spectrum that was similar to that of the benzal derivative of phenylacetonitrile (VI). In Table I are listed some of the more significant infrared absorption bands for nitriles V and VI.



$$\underset{\displaystyle CN}{C_6H_5C}{=}CHC_6H_5$$

VI

The bands at 4.5 and 4.46 μ are ascribed to the nitrile group since Bellamy[12] gives 4.45–4.5 μ for the nitrile group in α,β-unsaturated alkyl nitriles. The bands at 14.32 and 14.33 μ are evidently due

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[1] Supported by the Office of Ordnance Research, U. S. Army.

[2] J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, **22**, 355 (1957). For an earlier communication, see C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **21**, 382 (1956).

[3] C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 906 (1957).

[4] C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 1246 (1957).

[5] C. R. Hauser, J. K. Lindsay, and D. Lednicer, *J. Org. Chem.*, **23**, 358 (1958).

[6] D. Lednicer, J. K. Lindsay, and C. R. Hauser, *J. Org. Chem.*, **23**, 653 (1958).

[7] In a preliminary communication [C. R. Hauser, J. K. Lindsay, D. Lednicer, and C. E. Cain, *J. Org. Chem.*, **22**, 717 (1957)] the S_N2', displacement was assumed to occur with the cyanide ion to form the 2-methylcyano structure but this structure was soon discarded in favor of structure IV; see refs. 5 and 6. Evidence for the latter structure has been independently obtained by J. M. Osgerby and P. L. Pauson, see ref. 8.

[8] J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.*, 656 (1958); see also J. M. Osgerby and P. L. Pauson, *Chem. and Ind.*, 196 (1958).

[9] P. L. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson, and G. M. Whitman, *J. Am. Chem. Soc.*, **79**, 3416 (1957).

[10] K. L. Rinehart, Jr., Ronald J. Curby, Jr., and Phillip E. Sokol, *J. Am. Chem. Soc.*, **79**, 3420 (1957).

[11] See H. M. Crawford, *J. Am. Chem. Soc.*, **56**, 139 (1934).

[12] See L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

to the monosubstituted phenyl group since Bellamy[12] gives the same value for this group. The band at 9.02 μ in nitrile V is indicative of an unsubstituted ferrocene ring.[13]

TABLE I

Infrared Bands of Nitriles V and VI (μ)

V	VI
4.50	4.46
6.81	6.69
6.90	6.88
7.25	7.23
9.02	—
14.32	14.33

EXPERIMENTAL

2-Ferrocenyl-3-phenylacrylonitrile (V). To 400 ml. of absolute ethanol was added approximately 0.01 g. (0.004 mole) of sodium metal. When the sodium had disappeared and the evolution of hydrogen ceased, 1 g. (0.005 mole) of ferrocenylacetonitrile was added, followed by 1.1 g. (0.01 mole) of freshly distilled benzaldehyde. The resulting red solution was refluxed for 6 hr. The volume of the solvent was then reduced *in vacuo* to about 50 ml. To the deep red solution there was added 100 ml. of ethyl ether and 200 ml. of water. The two layers were separated. The aqueous layer was extracted twice with 100 ml. portions of ether, and the extracts combined with the original ether layer. After drying over magnesium sulfate, the solution was evaporated almost to dryness. The residue was recrystallized from *n*-hexane to give 1.3 g. (80%) of the bronze-colored platelets of 1-ferrocenyl-2-phenylacrylonitrile (V), m.p. 112–114° (uncorr.). Further recrystallization from hexane did not raise the melting point.

Anal.[14] Calcd. for $C_{19}H_{15}NFe$: C, 72.86; H, 4.82; N, 4.47; Fe, 17.83. Found: C, 72.80; H, 4.86; N, 4.45; Fe, 17.67.

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[13] See P. L. Pauson, *Quart. Revs.* (*London*), **9**, 391 (1955).

[14] Analysis by Galbraith Laboratories, Knoxville, Tenn.

Hydroxymethyl- and Formylferrocene with Oxidizing Agents. Bisferrocenylmethyl Ether[1]

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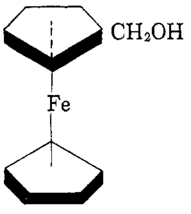
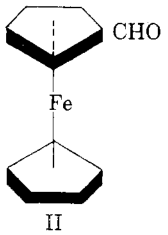
Received June 16, 1958

It has previously been shown that, although the iron in ferrocene is readily oxidized by ceric sulfate or ferric chloride,[2] hydroxymethylferrocene (I) can be oxidized to the corresponding aldehyde (II) with manganese dioxide without affecting the iron in the molecules.[3]

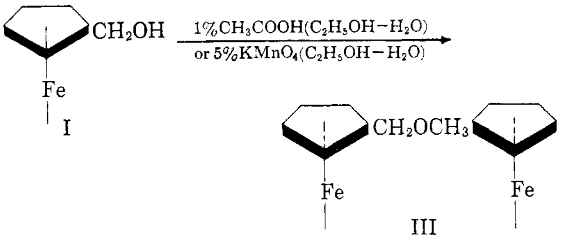


I



II

It has now been found that the iron in these molecules is also quite stable to oxidation toward dilute potassium permanganate.[4] Thus, on standing with a 5% solution of this reagent in aqueous ethanol at room temperature, alcohol I was converted, without affecting the iron, to a product that was evidently the ether III (87% crude yield). Actually the oxidizing agent was not required for this reaction, since the same product was obtained in equally good crude yield (88%) when alcohol I was refluxed in aqueous ethanol in the presence of a catalytic amount (1%) of acetic acid (Equation 1).



(1)

That the product was ether III was indicated not only by its analysis but also by its infrared absorption spectrum which supports the di-benzyl type ether structure. It gave a strong band at about 9.25μ for the carbon-oxygen ether linkage, but no hydroxyl or carbonyl group band. Bellamy[5] gives 8.7–9.4μ for the characteristic band of an aliphatic ether linkage. The compound also gave a sharp band at 3.24μ, a shoulder at 3.42μ and another sharp band at 3.53μ. The first band may be ascribed to an aromatic carbon-hydrogen linkage and the other two bands, to the methylenic carbon-hydrogen linkage. The values listed by Bellamy[5] for these linkages are 3.23μ, 3.42μ, and 3.51μ, respectively. The compound gave bands at 9.04 and 10.05μ which are characteristic of certain ferrocene derivatives having an unsubstituted ring.[6]

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[1] Supported by the Office of Ordnance Research, U. S. Army.

[2] G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, *J. Am. Chem. Soc.*, **74**, 2125 (1952).

[3] C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 906 (1957).

[4] A preliminary report was given in the latter part of the communication by C. R. Hauser, J. K. Lindsay, D. Lednicer, and C. E. Cain, *J. Org. Chem.*, **22**, 717 (1957).

[5] See L. J. Bellamy, *The Infra-red Spectra of Complex Molecules*, John Wiley and Sons, Inc., New York, N. Y., 1954.

[6] See P. L. Pauson, *Quart. Revs.* (*London*), **9**, 391 (1955).