

to the monosubstituted phenyl group since Bellamy¹² gives the same value for this group. The band at 9.02μ 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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DUKE UNIVERSITY
DURHAM, N. C.

(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 Ether¹

CHARLES R. HAUSER AND CHARLES E. CAIN

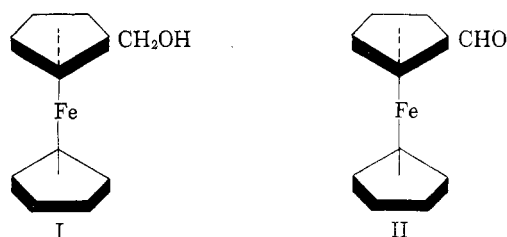
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It has previously been shown that, although the iron in ferrocene is readily oxidized by ceric sulfate or ferric chloride,² hydroxymethylferrocene (I) can be oxidized to the corresponding aldehyde

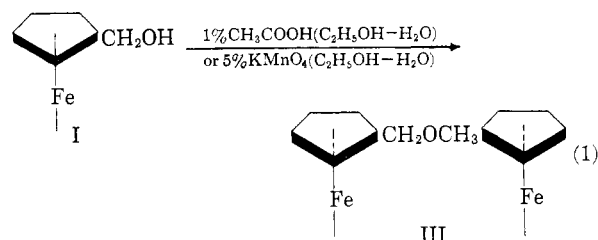
(1) Supported by the Office of Ordnance Research, U. S. Army.

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

(II) with manganese dioxide without affecting the iron in the molecules.³



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).



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. Bellamy⁵ gives $8.7\text{--}9.4\mu$ 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 Bellamy⁵ 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

(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).

Recently, Schlögl⁷ obtained ether III in 71% yield from alcohol I and phosphorus trichloride, in which reaction the chloride corresponding to alcohol I was presumably an intermediate. Also, other workers⁸ have reported the formation of ether III (54%) in an attempt to hydrogenate aldehyde II over Raney nickel.

Of the above methods for preparing ether III, only that involving the acid catalyzed reaction of alcohol I (see Equation 1) may be considered to follow an anticipated course.

With regard to the resistance of the iron in aldehyde II to oxidation, this aldehyde was recovered unchanged after heating a solution of it in an equal mixture of ethanol and water containing 2% potassium permanganate on the steam bath for 10 min. The aldehyde was also recovered after similar treatment employing a weakly acidic or weakly basic permanganate solution. This resistance to oxidation of the aldehyde group in II, as well as the iron, is of interest, since benzaldehyde undergoes oxidation to benzoic acid under similar conditions.⁹

However, aldehyde II was destroyed on heating an aqueous ethanolic solution of it containing alkaline permanganate for 2 hr. on the steam bath. These conditions produced a high melting material which was not the carboxylic acid corresponding to aldehyde II. As was anticipated, aldehyde II readily produced a colored (blue-green) ferricinium ion with 5% solutions of ceric sulfate, ferric chloride or ceric ammonium nitrate.

Also, aldehyde II in *n*-hexane evidently underwent oxidation on passing air through the solution, but the corresponding acid was not obtained. Instead, there was precipitated an unidentified brown¹⁰ powder which had the properties of an "inner salt" or "zwitter ion." Thus, it did not melt at 320°, and it was soluble in both dilute aqueous hydrochloric acid and dilute aqueous sodium hydroxide, and reprecipitated on careful neutralization (to pH 7), followed by the addition of acetone.

EXPERIMENTAL

Ferrocenylmethyl alcohol II with potassium permanganate. To 200 ml. of 5% solution of potassium permanganate in ethanol-water (50-50) was added 5 g. (0.023 mole) of ferrocenylmethyl alcohol (II). After stirring until the solid had disappeared, the resulting solution was allowed to sit for

(7) K. Schlögl, *Monatsh. Chem.*, **88**, 601 (1957).

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

(9) See R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, John Wiley & Sons, Inc., 4th Edition, New York, N. Y., 1956, p. 133.

(10) In reference 8 the statement is made that aldehyde II is sensitive to oxidation in dilute aqueous or in concentrated anhydrous hydrocarbon solutions to produce an amorphous brown powder.

12 days at room temperature. During this time, there was a slow discoloration of the permanganate solution (to greenish brown) which may have been due to oxidation of the ethanol. The remaining oxidizing agent was destroyed by the addition of saturated sodium bisulfite solution. The mixture was extracted twice with 150 ml. portions of ethyl ether and the extracts combined. The ethereal solution was dried over magnesium sulfate and most of the solvent removed by heating on the steam bath. The last traces of the solvent were removed *in vacuo* (water aspirator) to give 4.1 g. (87%) of a yellow solid, m.p. 126–129°, which was apparently the bisferrocenylmethyl ether III. A portion of the product was recrystallized from *n*-hexane to form orange crystals, m.p. 132–134°.

*Anal.*¹¹ Calcd. for C₂₂H₂₂OFe₂: C, 63.81; H, 5.35; Fe, 26.99. Found: C, 63.35; H, 5.59; Fe, 25.86.

Ferrocenylmethyl alcohol II with dilute acetic acid. In 80 ml. of a 1% solution of acetic acid in ethanol-water (50-50) was dissolved 2.5 g. (0.023 mole) of ferrocenylmethyl alcohol II. This solution was refluxed for 5 hr., cooled, and poured into 300 ml. of water. The resulting mixture was extracted three times with 100 ml. portions of ether and the extracts were combined. After drying over magnesium sulfate the ethereal solution was concentrated to a volume of about 50 ml. Approximately 100 ml. of hot *n*-hexane was added and the solution allowed to cool in a refrigerator. The resulting yellow precipitate was collected on a funnel and washed with *n*-hexane. There was obtained 2.2 g. (88%) of bisferrocenylmethyl ether III, m.p. 126–130°. Recrystallization from *n*-hexane gave orange crystals of the ether III, m.p. 132–134°.

*Anal.*¹¹ Calcd. for C₂₂H₂₂OFe₂: C, 63.81; H, 5.35; Fe, 26.99. Found: C, 64.01; H, 5.48; Fe, 26.63.

Samples of this product and of the product from the oxidation experiment above were shown to be identical by mixture melting point and infrared spectra.

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DUKE UNIVERSITY
DURHAM, N. C.

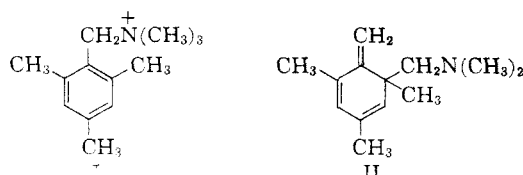
(11) Analyses by Galbraith Laboratories, Knoxville, Tenn.

Methiodide of *N*-(4-Benzyloxy-2,6-dimethylbenzyl)-*N,N*-dimethylamine. Attempted Rearrangement¹

DANIEL LEDNICER AND CHARLES R. HAUSER

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Recently² quaternary ammonium ion I has been shown to undergo with sodium amide in liquid ammonia the first phase of the ortho substitution rearrangement to form the *exo*-methyleneamine II, which exhibited certain interesting reactions.



(1) Supported by the Office of Ordnance Research, U.S.A.
(2) C. R. Hauser and D. N. Van Eenam, *J. Am. Chem. Soc.*, **78**, 5698 (1956).