After 2 hr, solid sodium carbonate was added until all the acid was neutralized, and the mixture was then evaporated to dryness. The residue, treated with 100 ml of water, was extracted with three 50-ml portions of chloroform. The chloroform extracts were washed with water, dried, and warmed to remove all volatile material. The residue was a viscous oil (4.0 g), which could be resolved into two spots ($R_f$ 0.54 and 0.83) on a thin-layer alumina chromatogram with benzene–chloroform (1:1) as the developing solvent. The oil was chromatographed through a 2.2 × 8.6-cm column of neutral alumina prepared from a slurry in benzene–chloroform (1:1). The elution solvents were 50 ml of benzene–chloroform (1:1), 25 ml of benzene–chloroform (1:4), 40 ml of ether–chloroform (1:1), 60 ml of chloroform, and 100 ml of chloroform–methanol. Fractions were monitored by thin-layer chromatography. A clean separation was effected, with the material with $R_f$ 0.53 coming out in the earlier fractions and the material with $R_f$ 0.83 coming out in the later fractions.

The $R_f$ 0.53 material (0.4 g of crystals) was recrystallized three times from chloroform–petroleum ether to give white crystals, mp 124–126°. A mull with mineral oil gave infrared absorption maxima at 3279, 1634, 1538, 1269, and 1242 cm$^{-1}$. Ultraviolet absorption in the 200–350 m$\mu$ region was nil. The sample for analysis, recrystallized further from chloroform–petroleum ether, had mp 125–127°.

*Anal.* Found: C, 64.44, 64.60; H, 7.00, 7.13; Br, 5.94, 6.19; N, 4.84, 4.65.

The $R_f$ 0.84 material (2.8 g of an oil) was brought out of benzene diluted with ether to give 2.2 g of white crystals XX. Three recrystallizations from acetone–ether furnished material with mp 135–136°.

*Anal.* Calcd for $C_{15}H_{20}BrNO_3$: C, 52.44; H, 5.97; Br, 23.35. Found: C, 52.38; H, 5.92; Br, 23.42.

A mull in mineral oil gave infrared absorption bands at 3344, 1631, and 1541 cm$^{-1}$. No ultraviolet absorption was detected between 200–350 m$\mu$. A 3% solution of the borohydride reduction product XX in deuteriochloroform showed nmr signals at 1.7–2.7 (7 H, complex, cyclohexane ring H's), 3.13 (1 H, broad, OH), 3.37 (3 H, s, $OCH_3$), 4.42 (2 H, d, $J$ = 4 cps, $ArCH_2$), 4.78 (1 H, complex, BrCH), 6.08 (1 H, broad, NH), and 7.27 ppm (5 s, H, ArH's).

**Registry No.**—IV, 16607-44-6; V, 16607-45-7; VI, 16607-46-8; VIII, 16607-47-9; VIII picrate, 16622-57-4; IX, 16607-48-0; IX 2,4-dinitrophenylhydrazone, 16607-49-1; X, 16607-51-5; X HCl, 16607-50-4; XIV, 16607-52-6; XV, 16607-53-7; XX, 16607-54-8.

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## Nuclear Magnetic Resonance of 1-Methylimidazole Methiodide. A Correction

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In the course of our studies in imidazoles, we reinvestigated the nmr spectrum of 1-methylimidazole methiodide (1), which had been reported in 1965.[1] In contrast to the earlier paper, we have now found that the aromatic protons at C-4 and C-5 absorb at a lower field (H-2, $\tau$ 1, 22 ppm, s, broad; H-4,5, $\tau$ 2.47 ppm, d, $J$ = 1.7 Hz; in water, DSS = 10) than in 1-methylimidazole itself (2.59, 3.14, and 2.95 ppm; in $CDCl_3$, TMS = 10).[2] The chemical shifts of the corresponding protons in pilocarpine methiodide ($\tau$ 1.27 and 2.55 ppm in water) are of the same order. These data are in accord with a report of Mannschreck, *et al.*,[3] that the aromatic protons of imidazole are shifted downfield when the nitrogen is protonated in strong acids. Further we succeeded in splitting the N-methyl signal of **1** into a doublet with $J_{NCH_3,H\text{-}2}$ = 0.45 Hz as anticipated by Mannschreck.[3] The coupling between the N-methyl group and H-2 was confirmed by double resonance.

**Registry No.**—**1**, 16727-92-7.

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[1] C. G. Overberger, J. C. Salomone, and S. Yaroslavsky, *J. Org. Chem.*, **30**, 3580 (1965).

[2] G. S. Reddy, R. T. Hobgood, Jr., and J. H. Goldstein, *J. Amer. Chem. Soc.*, **84**, 336 (1962).

[3] A. Mannschreck, W. Seitz, and H. A. Staab, *Ber. Bunsenges. Phys. Chem.*, **67**, 470 (1963).

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## Ozonations of Olefinic Ferrocenes[1]

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The relative ease with which ferrocene may be oxidized presents serious difficulties in projected oxidative transformations of ferrocene derivatives. Thus, for example, in our laboratory we have tried a number of well-established procedures for carbon–carbon double-bond cleavage only to find that destruction of the ferrocene nucleus also occurred. In this Note, we report the results of our study on the ozonation of a series of model olefinic ferrocenes.

Our successful ozonation technique lay in the careful treatment of the olefinic ferrocene with the exact molar equivalent of ozone required for reaction with the alkenyl linkage. For this purpose preparation and use of standardized solutions of ozone in anhydrous ether was found to be satisfactory.

With the monosubstituted olefin, vinylferrocene (**1**), ozonization proceeded smoothly, giving hydroxymethylferrocene (**2**) in 74% yield upon reduction with lithium aluminum hydride. Hydrolysis in the presence of zinc dust provided ferrocenecarboxaldehyde (**3**) in 32% yield, while use of the trimethyl phosphite work-up procedure gave the aldehyde in 85% yield. Three examples of disubstituted olefinic ferrocenes were investigated. Lithium aluminum hydride treatment of the ozonization mixture obtained from 1-ferrocenyl-1-phenylethene (**4**) gave ferrocenylphenylcarbinol (**5**) in 51% yield. Benzoylferrocene (**6**) was produced by hydrolysis and by reaction with trimethyl phosphite in yields of 42 and 45%, respectively. Hydride reduction of the mixture obtained from ozonization of cinnamoylferrocene (**7**) gave the new glycol, 1-ferrocenyl-1,2-dihydroxyethane (**8**), in 36% yield, but no ferrocene compound could be detected after the zinc–water treatment

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[1] (a) Taken in part from the dissertation submitted by W. D. L. to the Graduate School, University of South Carolina, May 1967, in partial fulfillment of the requirements for the Master of Science degree. (b) For a previous paper related to the present work, see S. I. Goldberg, W. D. Loeble, and T. T. Tidwell, *J. Org. Chem.*, **32**, 4070 (1967).