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The Reaction of Methylferrocene with Manganese(III) Acetate

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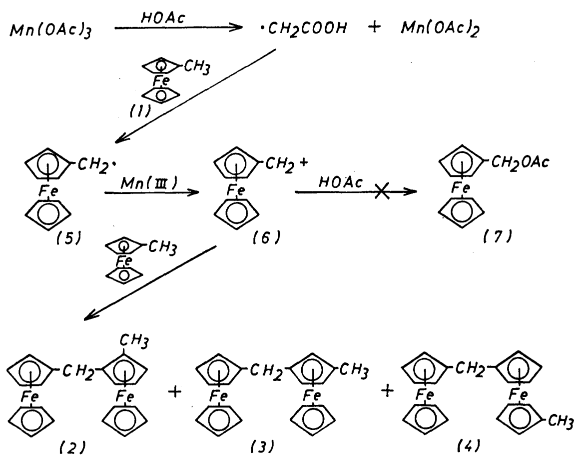
Synopsis. The oxidation of methylferrocene with manganese(III) acetate in acetic acid yielded three products which arose from the ferrocenylmethylation of methylferrocene. The reaction of methylferrocene with manganese(III) acetate in presence of styrene was also examined.

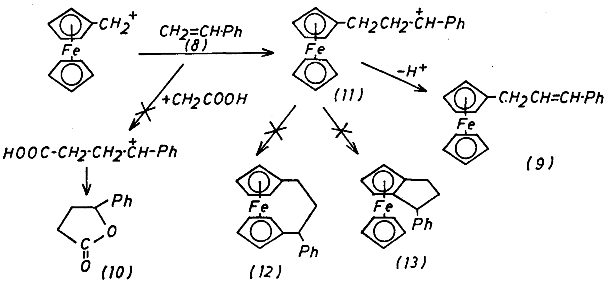
Previously, Heiba *et al.*[1] have reported the oxidation of aromatic hydrocarbons by manganese(III) acetate in acetic acid; they suggested that a free radical mechanism involving the selective generation and oxidation of organic free radicals is present. For example, the reaction of toluene with manganese(III) acetate led to the formation of a mixture of benzyl acetate, methylbenzyl acetate, and tolylacetic acid. The present investigation deals with the manganese(III) acetate oxidation of methylferrocene (**1**).

Results and Discussion

In a solution of acetic acid containing manganese(III) acetate and anhydrous potassium acetate, **1** was heated at 120 °C until the dark brown color of Mn(III) ion disappeared. Ferrocenyl(2-methylferrocenyl)methane (**2**), ferrocenyl(3-methylferrocenyl)methane (**3**), and ferrocenyl(1′-methylferrocenyl)methane (**4**) were obtained as the products.

In general, the thermolysis of manganese(III) acetate leads almost exclusively to the formation of $\cdot CH_2COOH$ radicals.[1,2] On the other hand, ferrocene does not appear to be particularly susceptible to attack by free radicals.[3] Consequently, in the reaction of **1** with manganese(III) acetate, the attack by the $\cdot CH_2COOH$ radical most likely occurs at the methyl group of **1**; this mechanism is shown in Scheme 1. Kochi *et al.*[4] suggested that the $\cdot CH_2COOH$ radical is oxidized relatively slowly to the correposnding carbonium ion, in contrast to the benzylic radical. In the oxidation of **1** with manganese(III) acetate, the formation of **2**, **3**, and **4** indicates therefore that the $\cdot CH_2COOH$ radical reacts more rapidly with **1** than the radical is oxidized by Mn(III) and the ferrocenylmethyl radical (**5**) is oxidized somewhat more rapidly to the corresponding carbonium ion (**6**) than the $\cdot CH_2COOH$ radical is oxidized by Mn(III). Furthermore, the absence of the formation of ferrocenylmethyl acetate (**7**), which is an expected side product in this reaction, indicated that the **6** carbonium ion reacts more rapidly with **1** than with acetic acid.





Heiba and Dessau[5] described a reaction of olefins with aromatic ketones such as acetophenone in the presence of manganese(III) acetate, leading to the formation of cyclized ketones together with noncyclized products. We have now found that the reaction of **1** with manganese(III) acetate in the presence of styrene (**8**) led to the formation of a noncyclized product (**9**), together with **2**, **3**, and **4**. The formation of **9** and the absence of γ-lactone (**10**), which is an expected product in the reaction, indicate that the **6** carbonium ion adds to the olefin more quickly than the $\cdot CH_2COOH$ radical adds to the olefin and that the H^+ abstraction from an intermediate (**11**) is faster than the intramolecular cyclization of **11** to **12** or **13**.

Experimental

Materials. All the melting points are uncorrected. The IR and mass spectra were measured using a Hitachi 215 spectrophotometer and a Model RMU-6M mass spectrometer at 70 eV. The NMR spectra were obtained on a Hitachi Model R-22 (90 MHz), using TMS as an internal standard.

The preparation of the following compounds has already been reported: methylferrocene (**1**)[6] and manganese(III) acetate dihydrate.[1]

*The Reaction of Methylferrocene (**1**) with Manganese(III) Acetate.* A mixture of **1** (3.0 g, 15 mmol) and anhydrous potassium acetate (7.4 g) in 75 ml of acetic acid was heated at 120 °C under nitrogen with manganese(III) acetate dihydrate (4.0 g, 15 mmol) until the brown color of Mn(III) ion disappeared (14 h). The reaction mixture was diluted with water and extracted several times with ether. The ether extracts were then dried over anhydrous magnesium sulfate and evaporated. The residue was chromatographed on silica gel with hexane as the eluent.

The first elution with hexane gave 1.82 g of the starting material (**1**).

The second elution with hexane–benzene (1 : 1) gave 0.38 g (6.4%[7]) of **2**, mp 95—97 °C (ethanol). Found: C, 66.21; H, 5.43%. Calcd for $C_{22}H_{22}Fe_2$: C, 66.37; H, 5.56%; mol wt, 398. IR: 3090, 2980, 2920, 1100, 1000, and 910 cm^{-1}. NMR ($CDCl_3$): δ 1.90 (3H, s, CH_3), 3.33 (2H, s, CH_2), 3.97, 4.01, and 4.05 ppm (17H, m, Cy protons). MS: *m*/*e* 398 (M^+ for $C_{22}H_{22}Fe_2$). The physical constants and IR and NMR spectra were identical with those of ferrocenyl(2-methylferrocenyl)methane (**2**), which was prepared by the reduction with $LiAlH_4$–$AlCl_3$ of ferrocenyl 2-methylferrocenyl ketone (mp 102—103 °C).

The third elution with benzene–hexane (1 : 1) gave 0.47 g (7.8%) of **3**, mp 83—85 °C (ethanol). Found: C, 66.22; H, 5.45%. Calcd for $C_{22}H_{22}Fe_2$: C, 66.37; H, 5.56%, mol wt, 398. IR: 3090, 2980, 2920, 1100, 1000, 920, and 910 cm^{-1}. NMR ($CDCl_3$): δ 1.87 (3H, s, CH_3), 3.28 (2H, s, CH_2), 3.96, 4.03, and 4.07 ppm (17H, m, Cy protons). MS: *m*/*e* 398 (M^+ for $C_{22}H_{22}Fe_2$). The **3** compound is identical in all respects with ferrocenyl(3-methylferrocenyl)methane, which was prepared by the reduction of ferrocenyl 3-methylferrocenyl ketone (mp 90—92 °C) with $LiAlH_4$–$AlCl_3$.

The following elution with benzene–hexane (1 : 1) gave 0.43 g (7.0%) of **4**, mp 85—97 °C (ethanol). Found: C, 66.31; H, 5.48%. Calcd for $C_{22}H_{22}Fe_2$: C, 66.37; H, 5.56%; mol wt, 398. IR: 3090, 2980, 2920, 1100, 1000, and 910 cm^{-1}. NMR ($CDCl_3$): δ 1.91 (3H, s, CH_3), 3.36 (2H, s, CH_2), 3.97, 4.02, and 4.07 ppm (17H, m, Cy protons). MS: *m*/*e* 398 (M^+ for $C_{22}H_{22}Fe_2$). The **4** compound is identical in all respects with ferrocenyl(1′-methylferrocenyl)methane, which was prepared by the reduction of ferrocenyl 1′-methoxycarbonylferrocenyl ketone (mp 180—182 °C)[8] with $LiAlH_4$–$AlCl_3$.

*The Reaction of Methylferrocene (**1**) with Manganese(III) Acetate in the Presence of Styrene.* A mixture of **1** (3.0 g, 15 mmol), styrene (1.54 g, 15 mmol), and anhydrous potassium acetate was heated at 120 °C under nitrogen with manganese(III) acetate dihydrate (4.0 g, 15 mmol) until the brown color of Mn(III) ion disappeared (10 h). The isolation of the products in the same manner as was used for the oxidation of **1** with manganese(III) acetate gave **2** (mp 95—97 °C, 0.35 g, 6.0%), **3** (mp 83—85 °C, 0.41 g, 7.0%), **4** (mp 85—87 °C, 0.38 g, 6.3%), and **9** (mp 68—70 °C, 0.52 g, 11.5%).

The **9** compound is identical in all respects with 3-ferrocenyl-1-phenyl-1-propene, which was prepared by the reduction of cinnamoylferrocene (mp 139—140 °C)[9] with $LiAlH_4$–$AlCl_3$. Found: C, 75.38; H, 5.83%. Calcd for $C_{19}H_{18}Fe$: C, 75.51; H, 6.00%; mol wt, 3.02. IR: 3090, 2980, 2920, 1100, 1000, 905, and 960 cm^{-1} (trans –CH=CH–). NMR ($CDCl_3$): δ 3.21 (2H, t, CH_2), 4.10 (5H, s, Cy protons), 4.16 (4H, br-s, Cy protons), 6.40 (1H, m, J=15 Hz, –CH=C–Ph), and 7.20—7.40 ppm (6H, m, –C=CH–Ph+Ph protons). MS: *m*/*e* 302 (M^+ for $C_{19}H_{18}Fe$).

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