Abnormal Reaction of Ferrocene with Unsaturated Dibasic Acid Chloride and NMR Spectra of Ferrocene Derivatives

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Treatment of ferrocene (10.0 g., 0.054 mol.) with fumaryl chloride (4.1 g., 0.027 mol.) in presence of aluminum chloride (7.2 g., 0.054 mol.) in methylene chloride (150 ml.) gave a mixture from which were isolated a saturated compoud, 1, 2-diferrocenoylethane (I, 2.3 g.), orange needles, m. p. 185∼186°C, not depressed on admixture with an authentic specimen(1), and β-ferrocenoylpropionic acid (4.5 g.). The expected *trans*-diferrocenoylethylene was not obtained as in the case of benzene(2). Found: C, 63.58: H, 4.83. Calcd. for $C_{24}H_{22}O_2Fe_2$: C, 63.44; H, 4.85%.

Dihydropyridazine derivative of I; brown needles, m. p. 266°C (decomp.). Found: N, 6.27. Calcd. for $C_{24}H_{22}N_2Fe_2$: N, 6.22%. Infrared, ultraviolet and NMR spectra of I are identical with those of 1, 2-diferrocenoylethane(1); IR, 1660 cm^{-1} (>CO) (KBr), UV (95% ethanol), 460 mμ (ε, 910). The NMR spectrum of I contains one singlet at $\tau=6.86$ (methylene protons), and another singlet at $\tau=5.76$ (unsubstituted ring protons) and two widely separated triplets at $\tau=5.51$ and 5.18; $J=1.64$ c.p.s. (substituted ring protons).

Under the same conditions as above 1, 2-diferrocenoylpropane (II, 1.8 g.) and 1-methyl-2-ferrocenoylpropionic acid (III, 5.2 g.) were obtained by reaction of ferrocene (10 g.) with citraconyl chloride (4.5 g.).

2, 4-Dinitrophenylhydrazone of II; purple crystals, m. p. 234°C. Found: C, 56.84; H, 4.15; N, 8.53. Calcd. for $C_{31}H_{28}O_5N_4Fe_2$: C, 57.41; H, 4.32; N, 8.64%. IR, 1665 (>CO), 1615 (>C=N–), 1518, 1500, 1320 cm^{-1} ($-NO_2$) (KBr). *p*-Bromophenacyl ester of III (IV); light orange needles, m. p. 149∼150°C. Found: C, 55.71; H, 4.24. Calcd. for $C_{23}H_{21}O_4BrFe$: C, 55.53; H, 4.23%. IR; 1740 (ester CO), 1715 (PhCO–), 1665 cm^{-1} (FcCO–) (KBr). UV (95% ethanol), 464 mμ (ε, 435). The NMR spectrum of IV contains three singlets at $\tau=5.76$, 5.51 and 5.20 (ferrocene ring protons), with an expected doublet at $\tau=8.66$; $J=6.22$ c.p.s. (methyl protons) and multiplet at $\tau=6.60\sim7.16$ (methylene protons and a proton at a tertiary carbon). Besides these it contains two quartets at $\tau=4.70$; $J=8.2$ c.p.s. and 2.32; 8.53 (benzene ring and methylene protons respectively) due to the phenacyl group.

It is a very interesting fact that the mono-substituted ferrocene derivatives (I and IV) have three peaks in the NMR specta. Rinehart(3) reported that the spectrum of 1, 1′-(tetramethylethylene)-ferrocene contains the expected methyl proton singlet at $\tau=8.74$, but the ring protons are found in two widely separated triplets at $\tau=6.11$ and 5.37; $J=1.6$ c.p.s.; and the considerable chemical shift is best explained as arising from the ring proton's unequal distance from the iron nucleus in a molecule where the rings are tilted. However, the chemical shift in our case is best explained as arising from the unequal inductive effect of carbonyl group on the ring protons. Thus α protons are assigned to the lower peak and β protons to the higher one in the substituted ring. This interpretation is in accord with the reactivity of acetylferrocene(4).

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