*Reaction of Ferrocene with Acyl Chloride**

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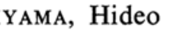
The Friedel-Crafts acylation of ferrocene with acetyl chloride was first reported by Woodward and his collaborators¹⁾. Subsequently the acylation of ferrocene has been reported on by many others. We should like to report briefly on the reactions of ferrocene with succinyl chloride and phenacetyl chloride.

Succinyl chloride is capable of Friedel-Crafts reaction with one or two molecules of aromatic hydrocarbon to give β-aroylpropionic acid or α, β-diaroylethane. The chloride can also react with aromatic hydrocarbons to form γ, γ-diarylbutyrolactone(2). We found that the chloride reacts with ferrocene to yield β-ferrocenoylpropionic acid (I), γ, γ-diferrocenylbutyrolactone (II) and 1, 2-diferrocenoylethane (III).

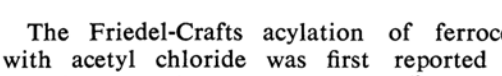
$FcCOCH_2CH_2COOH$

(I)



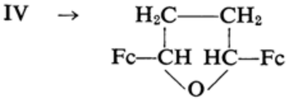
$(Fc)_2\underset{\text{O}}{C}CH_2\underset{\text{CO}}{CH_2}$

(II)



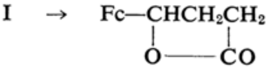
$FcCOCH_2CH_2COFc \rightarrow Fc\underset{\text{OH}}{CH}CH_2CH_2\underset{\text{OH}}{CH}Fc$

(III) (IV)



$IV \rightarrow$ 2, 5-diferrocenyltetrahydrofuran

(V)

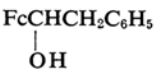


$I \rightarrow Fc\underset{\text{O}}{CH}CH_2\underset{\text{CO}}{CH_2}$

(VI)

$FcCOCH_2C_6H_5$

(VII)



$Fc\underset{\text{OH}}{CH}CH_2C_6H_5$

(VIII)

$FcCH{=}CHC_6H_5$

(IX)

Fc = Ferrocenyl ; FcCO = Ferrocenoyl**

Diketone III was reduced with lithium aluminum hydride to yield 1, 4-dihydroxy-1, 4-diferrocenylbutane (IV). IV easily gave 2, 5-diferrocenyltetrahydrofuran (V) with acid catalysts. β-Ferrocenoylpropionic acid (I) was readily lactonized by reduction with sodium borohydride in an ethanol solution, giving γ-ferrocenylbutyrolactone (VI). Similarly, phenylacetyl chloride reacts with ferrocene to give benzyl ferrocenyl ketone (VII) in a good yield. VII was reduced with lithium aluminum hydride to yield 1-ferrocenyl-2-phenylethanol (VIII) quantitatively. By treating VIII with

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1) R. B. Woodward et al., *J. Am. Chem. Soc.*, **74**, 2125 (1952).

2) V. Migrdichian, "Organic Syntheses", Vol. I, Reinhold Publ. Corp., New York (1957), p. 655.

** According to Chemical Abstracts' Nomenclature.

phosphorus pentachloride, 1-ferrocenyl-2-phenylethylene (IX) was obtained instead of the corresponding chloride.

The infrared spectra of II and VI exhibit strong absorption bands at 1770 and 1780 cm^{-1} (KBr) due to a γ-lactone group, and III and VII, at 1660 and 1665 cm^{-1} (KBr) due to a carbonyl conjugated with a ferrocene nucleus. These bands in III and VII are absent from IV and VIII, and new bands at 3400 and 3480 cm^{-1} (chloroform) due to a hydroxyl group appear in IV and VIII respectively. V shows no bands in the region for either hydroxyl or carbonyl. IX shows bands at 1640 and 960 cm^{-1} (KBr) due to a trans-disubstituted ethylene group (–CH=CH–). All these compounds have absorption bands at 1000 and 1110 cm^{-1}[3].

The visible spectra of II, IV, V, VI and VIII show absorption maxima similar to that of ferrocene itself at 445 (141), 443 (205), 443 (192), 442 (66.7) and 440 mμ (ε 104), and, on the other hand, the conjugate-expanded III and VII have absorption maxima at 458 (958) and at 462 mμ (ε 421) respectively in 95% ethanol which maxima correspond to that of acetylferrocene[4]. Strangely, IX showed also an absorption maximum at 460 mμ (ε 1000) in 95% ethanol.

Experimental

Reaction of Ferrocene with Succinyl Chloride.— To a vigorously stirred solution of ferrocene (10.0 g., 0.054 mol.) and aluminum chloride (7.2 g., 0.054 mol.) in methylene chloride (100 ml.) was slowly added a solution of succinyl chloride (4.2 g., 0.027 mol.) in the same solvent (50 ml.) under an atmosphere of nitrogen. After refluxing for 2 hr., the reaction mixture was cooled and poured onto crushed ice and water (100 ml.). On removal of the aqueous layer, the methylene chloride solution was separated into a neutral and an acidic fraction by extraction with 10% sodium carbonate (100 ml.). The acid fraction, on neutralization with 6 N hydrochloric acid, gave β-ferrocenoylpropionic acid (I, 1.0 g.) in leaflets, m. p. 164∼166°C (lit.[5] 166.5∼167.5°C). After removal of the solvent, the neutral fraction was dissolved in benzene, chromatographed on alumina and eluted as follows: (1) benzene (first portion) gave unchanged ferrocene (3.3 g.), and (2) benzene (second portion) gave γ-lactone (II) in the form of light orange needles, m. p. 165∼165.5°C (from ethyl acetate).

Found: C, 63.47; H, 4.87; Fe, 23.60, 23.86. Calcd. for $C_{24}H_{22}O_2Fe_2$: C, 63.44; H, 4.85; Fe, 24.60%.

(3) Ethyl acetate gave 1, 2-diferrocenoylethane (III, 2.1 g.) in the form of orange needles, m. p. 185∼186°C (from ethyl acetate).

Found: C, 63.34; H, 4.86. Calcd. for $C_{24}H_{22}\cdot O_2Fe_2$: C, 63.44; H, 4.85%.

The oxime of III, prepared with hydroxylamine hydrochloride and sodium acetate in methanol (2 hr. refluxing), m. p. 165∼166°C (decomp.) crystallized as needles (from methanol).

Found: N, 5.39. Calcd. for $C_{24}H_{24}O_2N_2Fe_2$: N, 5.74%.

1, 4-Dihydroxy-1, 4-diferrocenylbutane (IV).—A solution of III (1.0 g.) in anhydrous tetrahydrofuran (50 ml.) was gradually added to a stirred slurry of lithium aluminum hydride (0.5 g.) in the same solvent (50 ml.). The mixture was stirred for 2 hr. at room temperature. The excess of the hydride was destroyed with ethyl acetate. The organic layer was washed with distilled water several times and dried over anhydrous sodium sulfate. After removal of the solvent, the solid was crystallized from ethanol, affording IV (0.9 g.) in the form of yellow needles (from ethanol), m. p. 134∼135°C.

Found: C, 62.89; H, 5.93. Calcd. for $C_{24}H_{26}\cdot O_2Fe_2$: C, 62.88; H, 5.68%.

2,5-Diferrocenyltetrahydrofuran (V).—After reduction of III with lithium aluminum hydride as above, the tetrahydrofuran solution was shaken first with 10% sulfuric acid and then with water, and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was dissolved in benzene and chromatographed on alumina, and 2, 5-diferrocenyltetrahydrofuran (V) was crystallized quantitatively from ethanol, as yellow needles, m. p. 124.5∼125°C. The same material was also prepared by refluxing IV in acetic anhydride for 1 hr.

Found: C, 65.23; H, 5.56. Calcd. for $C_{24}H_{24}\cdot OFe_2$: C, 65.45; H, 5.45%.

γ-Ferrocenylbutyrolactone (VI).—A solution of β-ferrocenoylpropionic acid (I, 1.0 g.) and sodium borohydride (0.3 g.) in ethanol (50 ml.) was refluxed for 2 hr. After removal of the solvent, the residue was treated with water (30 ml.), acidified with concentrated hydrochloric acid (5 ml.), and warmed for 1 hr. on a water bath. The resulting solid was extracted with ethyl acetate. The extract was crystallized from *n*-pentane to yield γ-ferrocenylbutyrolactone (VI, 0.7 g.) in the form of yellow needles, m. p. 130∼131°C.

Found: C, 62.02; H, 5.08. Calcd. for $C_{14}H_{14}\cdot O_2Fe$: C, 62.24; H, 5.18%.

Benzyl Ferrocenyl Ketone (VII). — Phenacetyl chloride (8.3 g., 0.054 mol.) solution in methylene chloride (50 ml.) was added during 1 hr. to a stirred solution of ferrocene (10.0 g., 0.054 mol.) and aluminum chloride (7.2 g., 0.054 mol.) in methylene chloride (150 ml.) under an atmosphere of nitrogen. After refluxing for 5 hr., the reaction mixture was cooled and poured onto crushed ice and water (100 ml.). On removal of the aqueous layer, the methylene chloride solution was washed with 3 portions of water (50 ml.) and dried over anhydrous sodium sulfate. After removal of the solvent, the residue was dissolved in benzene and chromatographed on alumina. Elution with benzene and ethyl acetate gave material which crystallized from *n*-hexane. Benzyl ferrocenyl ketone (VII, 12.0 g., 73%) separated as orange-red needles, m. p. 128∼129°C.

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[3] 9-10 Rule, M. Rosenblum, *Chem. & Ind.*, **1958**, 953.

[4] K. Schlögel, *Monatsh. Chem.*, **88**, 601 (1957).

[5] K. L. Rinehart et al., *J. Am. Chem. Soc.*, **79**, 3423 (1957).

Found: 70.94; H, 5.29. Calcd. for $C_{18}H_{16}OFe$: C, 71.05; H, 5.26%.

The oxime prepared in methanol (2 hr. refluxing), crystallized from methanol in the form of orange-red needles, m. p. 142~143°C (decomp.).

Found: N, 4.32. Calcd. for $C_{18}H_{17}ONFe$: N, 4.38%.

1-Ferrocenyl-2-phenylethanol (VIII).—A solution of benzyl ferrocenyl ketone (VII, 5 g.) in anhydrous tetrahydrofuran (100 ml.) was added to a stirred slurry of lithium aluminum hydride (1 g.) in the same solvent (30 ml.). The mixture was stirred for 1 hr. under reflux after the addition was complete. The excess of the hydride was destroyed by the dropwise addition of moist ether, and the mixture was then acidified with 0.1 N sulfuric acid. The organic layer was washed with water (50 ml.) 3 times. After removal of the solvent, the solid residue was crystallized from *n*-pentane, affording 1-ferrocenyl-2-phenylethanol (VIII, 4.7 g., 93%), m. p. 82~83°C.

Found: C, 70.94; H, 5.29. Calcd. for $C_{18}H_{18}\cdot OFe$: C, 70.59; H, 5.88%.

1-Ferrocenyl-2-phenylethylene (IX). — 1-Ferrocenyl-2-phenylethanol (VIII, 1 g.) in anhydrous ether (50 ml.) was stirred under reflux with powdered phosphorus pentachloride (0.7 g.). After 5 hr. of stirring, the ether solution was decanted from the excess of the pentachloride, washed with 3 portions of water (50 ml.), and dried over anhydrous sodium sulfate. After evaporation of the ether, the solid residue was crystallized from *n*-pentane to give 1-ferrocenyl-2-phenylethylene (IX, 0.7 g., 80%) in the form of orange-red needles, m. p. 121~121.5°C.

Found: C, 74.64; H, 5.68. Calcd. for $C_{18}H_{16}Fe$: C, 74.98; H, 5.61%.

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