NONCONVENTIONAL FRIEDEL–CRAFTS CHEMISTRY.
VII. ON HOMOANNULAR AND HETEROANNULAR REACTIONS OF FERROCENE WITH BIFUNCTIONAL MOIETIES UNDER FRIEDEL–CRAFTS CONDITIONS

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Until now no investigators have reported the reaction of ferrocene with bifunctional molecules under Friedel–Crafts conditions. The utilization of ferrocene in the organic synthesis[1 – 9] and its uses in Friedel–Crafts chemistry[9 – 14], together with our interest in this area[15 – 18], prompted us to investigate the reaction of ferrocene with halo acid chlorides and α,β-unsaturated acid chlorides under different Friedel–Crafts conditions with the aim to employ these reactions in the syntheses of polycyclic ferrocene derivatives.

EXPERIMENTAL

Melting points are uncorrected. NMR Spectra were measured in $CDCl_3$ on EM-360 90-MHZ spectrometer and the chemical shifts are given in ppm (δ-scale) relative to TMS. Infrared spectra were recorded in KBr on a Pye–Unicam SP 200-G spectrophotometer. Isolation of products was achieved on a 20 × 15 cm glass plate covered with thin silica gel film. Elemental analyses were obtained on a Perkin–Elmer 240 C microanalyzer.

High-pressure liquid chromatography (HPLC) analyses were performed on a Hitachi apparatus (Japan) supplied with a variable-wavelength monitor (190 – 600 nm), with a sulfonated silica gel type column, Nucleosil 55 Å.

Reactions of Ferrocene with Bifunctional Molecules under Friedel–Crafts Conditions

A) In the presence of $AlCl_3/CH_3NO_2$ catalyst; General procedure: To a mixture of 0.012 mol of $AlCl_3$ in 25 ml CS_2 placed in two necked flask, 0.012 mol of nitromethane was added slowly while stirring. After stirring for one hour, 0.01 mol of ferrocene was added followed by the addition of 0.01 mol of the bifunctional molecule over a period of 1 h. The reaction mixture was stirred for an additional 2 h at room temperature, decomposed with 10% HCl solution, extracted with methylene chloride and the extract was washed with water, 10% sodium carbonate solution, again with water and dried over magnesium sulfate. The solvents were removed by distillation and the residue was subjected to quantitative HPLC analysis, chromatographed using silica gel on 20 × 15 cm glass plate and identified by ^1H NMR, IR spectroscopy and elemental analysis (Table I). The proportion of the products is given in Table II.

Table I
Physical data of ferrocene derivatives

Compound	M. p., °C Yield[a], %	Formula (M. w.)	Calculated/Found			IR, cm^{-1}	^{1}H NMR
			% C	% H	% Cl		
I	60 – 62 70	$C_{13}H_{13}OFeCl$	56.52 56.42	4.71 4.69	12.68 12.62	1 690 (C=O), 2 700 (CH aliph.), 3 100, 1 480, 1 390, 1 290, 1 120, 1 050, 1 000, 980, 900, 850, 830	3.85 – 4.18 m, 9 H[b]; 2.5 – 2.62 t, 2 H; 2.7 – 2.9 t, 2 H
II	80 – 83 10	$C_{13}H_{12}OFe$	65.00 65.10	5.00 5.12		1 745 (C=O), 2 700 (CH aliph.), 3 100, 1 480, 1 390, 1 290, 1 120, 1 050, 1 010, 980, 900, 850, 830	3.9 – 4.21 m, 8 H; 0.9 – 0.95 broad, 2 H; 1.2 – 1.5 m, 2 H
III	62 – 64 10	$C_{13}H_{12}OFe$	65.00 65.09	5.00 5.10		1 700 (C=O), 2 695 (CH aliph.), 3 100, 1 485, 1 395, 1 285, 1 120, 1 050, 1 010, 970, 895, 845	3.85 – 4.12 m, 8 H; 1 – 1.1 m, 2 H; 1.3 – 1.5 m, 2 H
IV	85 – 87 75	$C_{14}H_{15}OFeCl$	57.93 57.81	5.17 5.14	12.06 12.00	1 720 (C=O), 2 710, 2 730 (CH aliph.), 3 100, 1 495, 1 395, 1 290, 1 130, 1 050, 1 000, 980, 900, 850, 830	3.75 – 4.22 m, 9 H; 1.9 – 2.1 m, 2 H; 2.31 – 2.40 t, 2 H; 2.7 – 2.8 t, 2 H
V	120 – 122 15	$C_{14}H_{14}OFe$	66.14 66.90	5.51 5.49		1 715 (C=O), 2 700, 2 800 (CH aliph.), 3 100, 1 495, 1 390, 1 290, 1 130, 1 050, 1 000, 980, 900, 850	3.9 – 4.1 m, 8 H; 1.4 – 1.6 m, 2 H; 2 – 2.1 t, 2 H; 2.4 – 2.6 t, 2 H
VI	120 – 122 17	$C_{14}H_{14}OFe$	66.14 66.00	5.51 5.48		1 740 (C=O), 2 700, 2 800 (CH aliph.), 1 495, 1 395, 1 290, 1 130, 1 050, 1 000, 980, 900, 850	3.8 – 4.18 m, 8 H; 0.9 d, 3 H; 1.33 m, 1 H; 2.7 – 2.81 d, 2 H

TABLE I
(*Continued*)

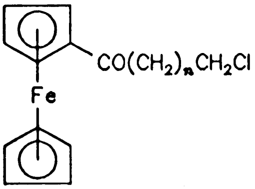
Compound	M. p., °C Yield[a], %	Formula (M. w.)	Calculated/Found			IR, cm^{-1}	^1H NMR
			% C	% H	% Cl		
VII	90 – 92 13	$C_{14}H_{14}OFe$	66.14 66.10	5.51 5.46		1 715 (C=O), 2 810 (CH aliph.), 3 100, 1 490, 1 400, 1 295, 1 135, 1 050, 1 020, 980, 900, 850	3.9 – 4.18 m, 8 H; 2 – 2.2 m, 2 H; 2.3 – 2.4 t, 2 H; 2.5 – 2.7 t, 2 H
VIII	75 – 77 13	$C_{14}H_{14}OFe$	66.14 66.00	5.51 5.48		1 720 (C=O), 2 750 (CH aliph.), 3 100, 1 495, 1 390, 1 290, 1 130, 1 050, 1 010, 985, 910, 860, 830	2.9 – 4.12 m, 8 H; 0.95 d, 3 H; 1.29 m, 1 H; 2.8 d, 2 H
IX[c]	68 – 70 70	$C_{14}H_{14}OFe$	66.14 66.10	5.51 5.49		1 690 (C=O), 2 710 (CH aliph.), 3 110, 1 490, 1 390, 1 290, 1 130, 1 050, 1 000, 980, 910, 870, 840	3.9 – 4.22 m, 9 H; 1.7 d, 3 H; 4.7 m, 1 H; 5.5 d, 1 H
X[c]	142 – 144 65	$C_{19}H_{16}OFe$	72.15 72.00	5.06 5.00		1 695 (C=O), 2 750 (CH aliph.), 3 045 (CH arom.), 3 100, 1 490, 1 390, 1 290, 1 140, 1 055, 1 010, 980, 920, 890, 845	3.85 – 4.22 m, 9 H; 4.7 d, 1 H; 5.5 d, 1 H; 7.5 – 7.9 m, 5 H
XI	65 – 67 7	$C_{19}H_{16}OFe$	72.15 72.10	5.06 5.10		1 745 (C=O), 2 740, 2 800 (CH aliph.), 3 050 (CH arom.), 3 110, 1 495, 1 395, 1 295, 1 135, 1 055, 1 010, 990, 910, 855	3.9 – 4.22 m, 8 H; 1.32 t, 1 H; 2.7 – 2.81 d, 2 H; 7.6 – 8 m, 5 H
XII[c]	58 – 60 13	$C_{19}H_{16}OFe$	72.15 72.13	5.06 5.00		1 718 (C=O), 2 800 (CH aliph.), 3 055 (CH arom.), 3 100, 1 500, 1 390, 1 295, 1 130, 1 060, 1 010, 990, 900, 870, 820	3.9 – 4.12 m, 8 H; 1.22 m, 1 H; 2.8 d, 2 H; 7.7 – 8 m, 5 H

[a] Calculated by HPLC; [b] ferrocenyl protons; [c] ^1H NMR measured in $CDCl_3/CF_3COOH$.

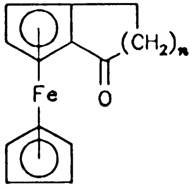
TABLE II
Reactions of ferrocene with various bifunctional moieties under different Friedel–Crafts conditions[a]

Experiment	Bifunctional compound	Observed products[f] (yield, %)
1[b,d]	$ClCH_2CH_2COCl$	*I* (70), *II* (10), *III* (10)
2[b,e]	$ClCH_2CH_2COCl$	*I* (20), *II* (30), *III* (35)
3[b,d]	$ClCH_2CH_2CH_2COCl$	*IV* (75), *V* (15), *VII* (13)
4[c,e]	$ClCH_2CH_2CH_2COCl$	*V* (30), *VI* (17), *VII* (30), *IV* (5), *VIII* (13)
5[c,d]	$CH_3CH=CHCOCl$	*IX* (70), *VI* (10), *VIII* (12)
6[b,e]	$CH_3CH=CHCOCl$	*VI* (35), *VIII* (25), *IX* (20)
7[b,d]	$PhCH=CHCOCl$	*X* (65), *XI* (7), *XII* (13)
8[b,e]	$PhCH=CHCOCl$	*X* (10), *XI* (38), *XII* (27)

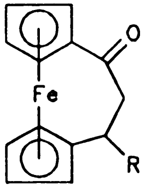
[a] Solvent CS_2, temperature 25 °C, reaction time 3 h. Ratio ferrocene/bifunctional compound/catalyst: [b] 0.01 : 0.01 : 0.012; [c] 0.01 : 0.01 : 0.12. Catalyst: [d] $AlCl_3/CH_3NO_2$; [e] $AlCl_3$; [f] calculated from HPLC.



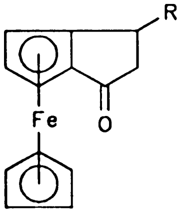
I, *n* = 1
IV, *n* = 2



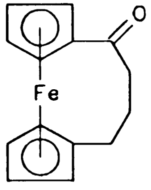
II, *n* = 1
V, *n* = 2



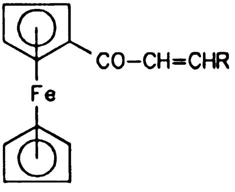
III, R = H
VIII, R = CH_3
XII, R = C_6H_5



VI, R = CH_3
XI, R = C_6H_5



VII



IX, R = CH_3
X, R = C_6H_5

B) *In the presence of $AlCl_3$ catalyst; General procedure*: A two necked flask was charged with 0.012 mol $AlCl_3$ and 25 ml dry CS_2. To this mixture 0.01 mol of ferrocene was added followed by dropwise addition of 0.01 mol of the bifunctional compound. The reaction mixture was processed as described previously and the same methods of the products identification were applied. The products are characterized in Table I and their proportion given in Table II.

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