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Nitroalkenylferrocene. III.⁽¹⁾ Condensation Reaction of Acetylferrocene Using Lewis Acid and Cyclic Amine

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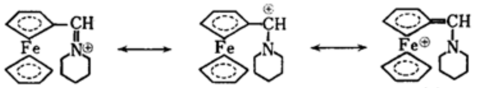
Acetylferrocene reacted with nitromethane and morpholine in the presence of titanium(IV) chloride to give a Mannich base, 2-ferrocenyl-2-morpholino-1-nitropropane (**7**), whose sodium salt (**8**) was then converted to 2-ferrocenyl-1-nitropropene (**9**) by acidifying it with hydrochloric acid. In the presence of aluminum chloride in place of titanium(IV) chloride, acetylferrocene as well as 1,1′-diacetylferrocene dimerized to form α,β-unsaturated ketone, (**10**) or (**11**).

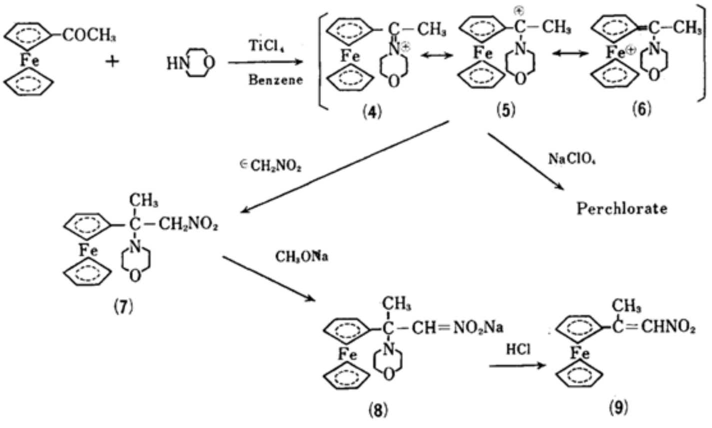
In a previous paper[2] it has been reported that a condensation reaction of formylferrocene with nitroalkane and cyclic amine gave a Mannich base through an intermediacy involving an immonium ion-carbonium ion resonance[3] participated with ferrocene nuclei.



(1) (2) (3)

The fact that the Mannich base was the main product indicates that the carbonium-ion structure (**2**) is the most favorable and that it is predominantly attacked by a carbanion generated from nitroalkane.

However, neither acetylferrocene nor benzoylferrocene reacted under similar conditions. In these cases it can be assumed that the methyl or phenyl group on a carbonyl carbon may sterically prevent the formation of enamine. The procedure reported by White and Weingarten[4] for the preparation of enamines from sterically-hindered ketones in the presence of Lewis acid was applied to the condensation of acylferrocene with nitroalkane, using titanium(IV) chloride as the condensing agent. By this procedure, acetylferrocene reacted with morpholine to give an enamine when a solution of titanium(IV) chloride in benzene was added to a benzene solution of acetylferrocene and an excess of morpholine. A part of the enamine thus formed was isolated as a perchlorate, which then crystallized in fine, dark red scales. In the IR spectrum of the perchlorate, a characteristic absorption band of the $-\mathrm{C}{=}\overset{+}{\mathrm{N}}-$group was observed at 1613 cm^{-1}.[5] When nitromethane was added to the reaction mixture containing the enamine, 2-



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[1] Part II: M. Shiga, H. Kono, I. Motoyama and K. Hata, This Bulletin, **42**, 798 (1969).

[2] M. Shiga, H. Kono, I. Motoyama and K. Hata, *ibid.*, **41**, 1897 (1968).

[3] R. Oda, *Chemistry (Kagaku)*, **18**, 127 (1963).

[4] W. A. White and H. Weingarten, *J. Org. Chem.*, **32**, 213 (1967).

[5] M. Sato, H. Kono, M. Shiga, I. Motoyama and K. Hata, This Bulletin, **41**, 252 (1968).

TABLE 1. THE SELF-CONDENSATION OF ACETYLFERROCENE

Reaction temp.: room temperature (15°C).
Solvent: benzene.

Exp. No.	$FcCOCH_3$	Morpholine	$AlCl_3$	Reaction time	Yield of condensation product	Recovery of $FcCOCH_3$
1	1.0 g	5.0 g	0.5 g	5 hr	0.3 g (31.2%)	0.42 g (42%)
2	11.4	22.0	8.3	20	4.3 (39.2)	4.5 (39.4)
3	2.0	5.0	—	5	——	1.9 (95.0)
4	1.0	—	0.5	5	——	0.75 (75.0)
5*1	2.2	10.0	1.5	5	1.2 (56.7)	0.55 (25.0)
6*2	2.2	10.0	1.5	20	1.3 (61.3)	0.58 (26.0)

*1 2.0 g of acetic acid was added after the condensation reaction had been over.

*2 15 g of acetic anhydride was added after the condensation reaction had been over.

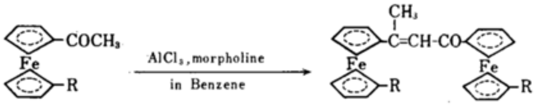
ferrocenyl-2-morpholino-1-nitropropane (**7**), mp 156—158°C, was obtained as orange crystals. When the Mannich base (**7**) was converted into its sodium salt (**8**) by sodium methoxide and then acidified with dilute hydrochloric acid, 2-ferrocenyl-1-nitropropene (**9**) was almost quantitatively obtained as violet crystals, mp 120—122°C.

The formation of an enamine from benzoylferrocene by a similar procedure was also proved by the isolation of its perchlorate. Nevertheless, no product was isolated from the reaction of the enamine with nitromethane. It is considered that the enamine from benzoylferrocene is far less reactive than that from acetylferrocene because of both the electronical stabilization and the steric hindrance by a phenyl group on it. Probably, a positive charge on the carbon atom bonded with a nitrogen atom in the enamine will be largely delocalized by the aid of the phenyl group attached to the carbonium ion; hence, the electrophilic nature of the enamine will be much reduced.

The IR spectrum of the nitroolefin (**9**) has an olefinic absorption band at 1606 cm^{-1} and characteristic asymmetric and symmetric nitro-stretching bands at 1508 cm^{-1} and 1320 cm^{-1} respectively. It is very interesting that the olefinic absorption band of 2-ferrocenyl-1-nitropropene (**9**) is 22 cm^{-1} lower than that of 2-ferrocenyl-1-nitroethylene, while that of 1-ferrocenyl-2-nitropropene, which is an isomer of **9**, is 24 cm^{-1} higher than that of 2-ferrocenyl-1-nitroethylene.[1] This observation suggests that the ethylenic bond of 2-ferrocenyl-1-nitroethylene may be much polarized *in situ*.

The NMR spectrum of **9** shows a singlet peak for methyl protons at τ 7.47, two singlet peaks at τ 5.82 and τ 5.48 for unsubstituted and substituted ferrocene ring protons respectively, and a singlet for vinyl proton at τ 2.69.

When aluminum chloride was used as a catalyst instead of titanium(IV) chloride, acetylferrocene dimerized in the presence of morpholine to form a self-condensation product, 1,3-diferrocenyl-2-buten-1-one (**10**), which had previously been reported to be formed from acetylferrocene by the reaction with potassium *t*-butoxide or sodium hydride.[6,7] By a similar reaction, 1,1′-diacetylferrocene also gave 1,3-bis(1′-acetylferrocenyl)-2-buten-1-one (**11**) in a moderate yield. Such a self-condensation reaction never occurs when only morpholine or aluminum chloride is used alone. The reaction conditions and the yields are listed in Table 1.



(**10**) R=H; (**11**) R=$COCH_3$

The reaction seems to proceed through an aldol condensation-type mechanism, and aluminum chloride may promote the polarization of the carbonyl group of acetylferrocene and facilitate the attack of a nucleophile on it. The yield of **10** increased upon the addition of acetic acid, acetic anhydride, or acetyl chloride after the primary condensation reaction was over. The acid was expected to be effective at the stage of the elimination of water molecule from the aldol-type condensation product[8] (Table 1, Exps. No. 5 and 6).

The IR spectrum of **11** has two kinds of carbonyl absorption bands, at 1664 cm^{-1} (acetyl group) and at 1644 cm^{-1} (α,β-unsaturated ketone), and an olefinic absorption band at 1597 cm^{-1}. The NMR spectra of the unsaturated ketones, (**10**) and (**11**), are presented in Table 2. The NMR spectrum of **10** shows the presence of three kinds of peaks for the substituted ferrocene ring protons, at τ 5.19, 5.40, and 5.54, with the relative intensities of 2, 2, and 4 respectively. The signals at τ 5.19 and 5.40

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6) P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, **1962**, 3880.

7) K. L. Rinehart, Jr., R. J. Curby, D. H. Gustafson, K. G. Harrison, R. E. Bozak and D. E. Bublitz, *J. Am. Chem. Soc.*, **84**, 3263 (1962).

8) A. C. Cope, *ibid.*, **59**, 2327 (1937).

TABLE 2. THE NMR SPECTRA OF α,β-UNSATURATED KETONES (τ-value, in $CDCl_3$)

	1,3-Diferrocenyl-2-buten-1-one (**10**)		1,3-Bis(1′-acetylferrocenyl)-2-buten-1-one (**11**)	
	τ-Value	Relative intensities	τ-Value	Relative intensities
Ferrocene ring protons				
Unsubstituted	5.81 (s)	5		
	5.84 (s)	5		
Substituted	5.19 (t)	2	5.23 (m)	6
	5.40 (t)	2	5.24 (m)	2
	5.54 (m)	4	5.50 (t)	8
Vinyl proton	3.27 (s)	1	3.38 (s)	1
Allylic methyl protons	7.44 (m)	3	7.49 (s)	3
Acetyl methyl protons			7.64 (s)	6

were assigned to α-protons to the carbonyl and olefinic substituents on the ferrocene rings respectively, and the signal at τ 5.54, to β-protons on the substituted ring. In the NMR spectrum of **11**, the signals at τ 5.23 and 5.34 were assigned to α-protons to the carbonyl and olefinic substituents respectively, and the signal at τ 5.50, to β-protons on the ferrocene ring.

Experimental

2-Ferrocenyl-2-morpholino-1-nitropropane (7). A solution of titanium(IV) chloride (3.5 g) in benzene (10 m*l*) was added, drop by drop, to a stirred solution of acetylferrocene (4.4 g) and morpholine (10 g) in benzene (20 m*l*) which had previously been cooled in an ice bath. In a little while, a yellowish-brown solid appeared to form a suspension in the reaction mixture. The suspension was stirred for 4 hr at room temperature, and then nitromethane (5 g) was added. After the reaction mixture had been stirred for another 16 hr, it was filtered and the residue on the filter was repeatedly washed with ether. The filtrate and the washing were combined and concentrated under reduced pressure at room temperature. From the concentrated solution 2-ferrocenyl-2-morpholino-1-nitropropane (**7**) was obtained as orange needles (0.58 g, 8.4%); mp 156—158°C. IR (KBr): 2850—3000 ($-CH_2-$), 1557 (NO_2) and 1105 cm^{-1} (C–O–C).

Found: C, 57.41; H, 6.42; N, 7.63%. Calcd for $C_{17}H_{22}N_2O_3Fe$: C, 57.03; H, 6.14; N, 7.82%.

A part of the yellowish-brown solid which separated in the initial reaction was dissolved in water to give a deep red solution. On the treatment of the aqueous solution with $NaClO_4$, dark red crystals of perchlorate were isolated. IR spectrum: 1613 cm^{-1} ($-\mathrm{C}{=}\underset{|}{\overset{+}{\mathrm{N}}}-$ group).

2-Ferrocenyl-1-nitropropene (9). Following the procedure described in a previous report,[1] 2-ferrocenyl-2-morpholino-1-nitropropane (0.13 g) was treated with sodium ethoxide in ethanol and then with dilute hydrochloric acid to afford 2-ferrocenyl-1-nitropropene (**9**), mp 120—122°C. The chromatographic purification of the nitroolefin (**9**) was carefully done because of its instability on alumina. IR (CCl_4): 1606 (C=C), 1508 (asym. NO_2) and 1319 cm^{-1} (sym. NO_2). NMR (in $CDCl_3$): τ 7.47 (singlet, 3H), 5.82 (singlet, 5H), 5.48 (singlet, 4H), 2.69 (singlet, 1H).

Found: C, 58.29; H, 5.08; N, 5.17%. Calcd for $C_{13}H_{13}NO_2Fe$: C, 57.59; H, 4.79; N, 5.16%.

1,3-Diferrocenyl-2-buten-1-one (10). (a) To a stirred mixture of 8.3 g (0.06 mol) of aluminum chloride and 50 m*l* of anhydrous benzene cooled in an ice bath there was added, drop by drop, a solution of 11.4 g (0.05 mol) of acetylferrocene and 22 g (0.25 mol) of morpholine in 70 m*l* of anhydrous benzene under an atmosphere of nitrogen. After the addition had been completed, the mixture was stirred for another 20 hr at room temperature. At the end of the reaction, the deep red reaction mixture was poured into water and the aqueous layer was extracted with benzene. The organic layer thus obtained was washed thoroughly with water and dried over anhydrous magnesium sulfate. The removal of the solvent left 8.8 g of an oil, which was then chromatographed on alumina with *n*-hexane-benzene (1 : 1). The first fraction gave 4.5 g of acetylferrocene, and the second fraction gave 4.3 g (39.2%) of 1,3-diferrocenyl-2-buten-1-one (**10**), which was recrystallized from methanol to yield fine, deep red crystals; mp 122—124°C (lit 123—124°C[7]). IR (KBr): 1638 (C=O) and 1585 cm^{-1} (C=C).

(b) A mixture of acetylferrocene (2.2 g, 0.01 mol), morpholine (10 g, 0.11 mol), and aluminum chloride (1.5 g, 0.01 mol) in anhydrous benzene (30 m*l*) was treated similarly. After it had been stirred for 18 hr at room temperature, 15 g (0.15 mol) of acetic anhydride was added, drop by drop, to the reaction mixture under ice cooling; the resulting reaction mixture was stirred for another 2 hr at room temperature. The treatment of the reaction mixture much as in the procedure (a) gave 0.58 g of acetylferrocene and 1.3 g (61.3%) of 1,3-diferrocenyl-2-buten-1-one (**10**).

1,3-Bis(1′-acetylferrocenyl)-2-buten-1-one (11). A reaction was carried out in the same way as has been described in the case of the procedure (a) above by using 1,1′-diacetylferrocene (1.20 g, 0.005 mol), morpholine (7.0 g, 0.08 mol), aluminum chloride (1.2 g, 0.001 mol), and anhydrous benzene (40 m*l*). After it had been stirred for 20 hr, the reaction mixture was poured into ice water and the aqueous layer was extracted with benzene. The organic layer was washed with water and dried over anhydrous magnesium sulfate. After the solvent had been removed by a rotatory evaporator, the deep red oily residue was carefully chromatographed on alumina with *n*-hexane, benzene and chloroform successively as the elution solvents. The first fraction, eluted with *n*-hexane-benzene, gave diacetylferrocene (0.7 g), while the second fraction, eluted with chloroform, gave a deep red oil which was then rechromatographed with *n*-hexane-benzene (1 : 2) to give 0.2 g (17%) of 1,3-bis(1′-acetylferrocenyl)-2-buten-1-one (**11**) as an oil. An analytical sample of **11** was obtained by repeated chromatography of the oily product on alumina. IR (liquid film): 1664 and 1644 (C=O), 1576 cm^{-1} (C=C).

Found: C, 63.94; H, 5.18%. Calcd for $C_{28}H_{26}O_3Fe$: C, 64.45; H, 4.98%.

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