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β-Ferrocenyl-α,β-unsaturated Ketones. II.[1] The Reduction of β-Ferrocenyl-α,β-unsaturated Ketones and Their Relative Reactivities

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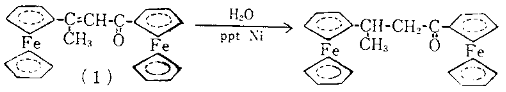
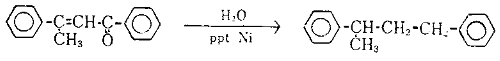
The catalytic reduction of several β-ferrocenyl-α,β-unsaturated ketones was investigated using Urushibara nickel A (U-Ni-A) or precipitated nickel (ppt-Ni) as the catalyst, and their relative reactivities toward the catalytic reduction were discussed in comparison with those of the phenyl analogs. Some anomalies observed in the NMR spectra of the reduction products was also discussed.

The preceding paper[1] in this series has reported on synthetic and spectroscopic studies of β-ferrocenyl-α,β-unsaturated ketones. This paper will deal with a study of the reduction of these unsaturated ketones and related compounds. Although a considerable number of works on the hydrogenation of α,β-unsaturated ketones have previously reported in some detail,[2-5] the reduction of the unsaturated ketones conjugated with the ferrocene group has scarcely been studied at all. Recently, the reduction of various organic compounds with water as a hydrogen donor in the presence of precipitated metal as a catalyst has been extensively investigated in our laboratory.[6,7] When 1,3-diferrocenyl-2-buten-1-one (**1**) was refluxed in a mixture of water and dioxane in the presence of precipitated nickel (ppt-Ni in abbreviation), 1,3-diferrocenyl-1-butanone was obtained almost quantitatively, while the reduction of dypnone (**2**) under the same conditions yielded 1,3-diphenylbutane exclusively. This interesting observation prompted us to more detailed investigations of the catalytic reduction of β-ferrocenyl-α,β-unsaturated ketones and related compounds in the hope of getting some information about the particular effect of the ferrocenyl group on the conjugated system.



(1)



(2)

Catalytic Hydrogenation of β-Ferrocenyl-α,β-unsaturated Ketones. β-Ferrocenyl-α,β-unsaturated ketones were hydrogenated with Urushibara nickel A (abbreviated as U-Ni-A)[8] under an atmospheric pressure of hydrogen at room temperature, using dioxane as the solvent. When the reaction was stopped after the absorption of equimolar hydrogen, the corresponding saturated ketones were obtained in most cases. The reaction conditions and the results are listed in Table 1. The products were purified by chromatography on alumina, and they were identified by means of elemental analyses and by a study of their IR and NMR spectra. The NMR data are summarized in Table 2.

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[1] Part I: H. Kono, M. Shiga, I. Motoyama and K. Hata, This Bulletin, **42**, 3273 (1969).

[2] M. Delepine and C. Hanegraaff, *Bull. Soc. Chim. Fr.*, [5] **4**, 2087 (1937).

[3] R. Cornubert and J. Phelisse, *C. R. Acad. Sci., Paris*, **227**, 1131 (1948).

[4] H. Adkins, *Ind. Eng. Chem.*, **32**, 1191 (1940).

[5] K. Hoshiai *et al.*, *Kogyo Kagaku Zasshi*, **59**, 236 (1956); **60**, 40, 253, 1150, 1527 (1957).

[6] K. Sakai and K. Watanabe, This Bulletin, **40**, 1548 (1967).

[7] K. Sakai, M. Ishige, H. Kono, I. Motoyama and K. Hata, *ibid.*, **41**, 1902 (1968).

[8] Y. Urushibara, S. Nishimura and H. Uehara, *ibid.*, **28**, 446 (1955).

TABLE 1. HYDROGENATION OF β-FERROCENYL-α,β-UNSATURATED KETONES IN THE PRESENCE OF U-Ni-A UNDER ORDINARY ATMOSPHERIC PRESSURE OF HYDROGEN
Solvent, dioxane; Shaking, 200 strokes/min

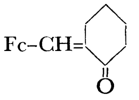
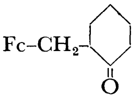
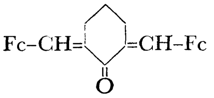
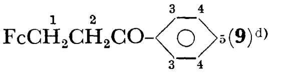
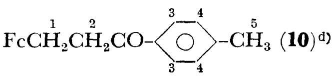
Compound	(g)	Cat. (g)	React. temp. (°C)	React. time (min)	Sol. (m*l*)	Product	Yield (%)
Fc-CH=CH-CO-CH_3 (**3**)	1.00	1.0	17.2	209	20	Fc-CH_2-CH_2-CO-CH_3 (**3a**)	80
	1.00	1.0	18.8	140	20		79
	0.50	0.5	22.4	80	10		85
	0.80	0.8	24.1	30	16		80
Fc-CH=CH-CO-C_2H_5 (**4**)	1.34	1.0	26.1	93	20	Fc-CH_2-CH_2-CO-C_2H_5 (**4a**)	77
Fc-CH=CH-CO-CH_2-$CH(CH_3)_2$ (**5**)	1.48	1.0	23.2	60	20	Fc-CH_2-CH_2-CO-CH_2-$CH(CH_3)_2$ (**5a**)	80
Fc-CH=CH-CO-CH=CH-Fc (**6**)	1.13	0.5	24.0	410	10	Fc-CH=CH-CO-CH_2CH_2-Fc (**6a**) Fc-CH_2CH_2-CO-CH_2CH_2-Fc (**6b**)	18.1 35.1
 (**7**)	0.74	0.5	23.0	415	10	 (**7a**)	41
 (**8**)	0.37	0.3	25.4	199	5	no reaction	
$Fc\text{-}\underset{CH_3}{C}{=}CH\text{-}CO\text{-}Fc$ (**1**)	1.50	0.5	20.0	280	10	$Fc\text{-}\underset{CH_3}{CH}\text{-}CH_2\text{-}CO\text{-}Fc$ (**1a**)	30

TABLE 2. NMR SPECTRA OF THE HYDROGENATION PRODUCTS OF β-FERROCENYL-α,β-UNSATURATED KETONES

Compound	τ Value (Intensity, signal pattern[a])						
	Unsubst. c.p. ring	Subst. c.p. ring	1	2	3	4	5
$Fc\overset{1}{CH_2}\overset{2}{CH_2}CO\overset{3}{CH_3}$ (**3a**)	5.91 (5H, s)	5.97 (4H, s)	7.39 (4H, s)		7.89 (3H, s)		
$Fc\overset{1}{CH_2}\overset{2}{CH_2}CO\overset{3}{CH_2}\overset{4}{CH_3}$ (**4a**)	5.89 (5H, s)	5.95 (4H, s)	7.38 (4H, s)		7.57 (2H, q)[b]	8.94 (3H, t)[b]	
$Fc\overset{1}{CH_2}\overset{2}{CH_2}CO\overset{3}{CH_2}\overset{4}{CH}\overset{5}{(CH_3)_2}$ (**5a**)	5.90 (5H, s)	5.97 (4H, s)	7.42 (4H, s)			7.98 (1H, m)	9.10 (6H, s)
$Fc\overset{1}{CH_2}\overset{2}{CH_2}COCH_2CH_2Fc$ (**6b**)	5.89 (5H, s)	5.94 (4H, m)	7.39 (8H, s)				
$Fc\overset{1}{CH_2}\overset{2}{CH_2}CO\overset{3}{CH}{=}\overset{4}{CH}Fc$ (**6a**)	5.85 (10H, s)	5.52 (4H, s) 5.88 (4H, m)	7.25 (4H, s)		2.49 (1H, d)[c]	3.65 (1H, d)[c]	
$Fc\overset{1}{CH_2}\overset{2}{CH}\text{-}CO\text{-}\overset{3}{(CH_2)_4}$ (**7a**)	5.90 (5H , s)	5.97 (4H, s)		7.07 (1H, m)	7.50—8.80 (10H, c)		
 (**9**)[d]	5.89 (9H, m)		7.25 (2H, m)	6.82 (2H, m)	2.05 (2H, m)	2.59 (3H, m)	
 (**10**)[d]	5.92 (9H, s)		7.26 (2H, m)	6.78 (2H, m)	2.14 (2H, d)[e]	2.79 (2H, d)[e]	7.64 (3H, s)

a) s: singlet, d: doublet, t: triplet, q:quartet, m: multiplet, c: complex.
b) *J*=7 Hz. c) *J*=16 Hz.
d) A preparation of this product will be reported in the following paper.
e) *J*=8 Hz.

The hydrogenation of 4-ferrocenyl-3-buten-2-one (**3**), 1-ferrocenyl-1-penten-3-one (**4**), and 1-ferrocenyl-5-methyl-1-hexen-3-one (**5**) gave the corresponding saturated ketones in good yields. The C=C stretching absorption bands at 1615 and 1591 cm^{-1} and the C=O stretching absorption bands at 1665 and 1684 cm^{-1}, due, respectively, to *s-trans* and *s-cis* isomerism observed in the spectrum of the unsaturated ketone (**3**), completely disappear in that of the hydrogenation product (**3a**), in which only the C=O absorption band at 1703 cm^{-1} appears.[1]

The hydrogenation of 1,5-diferrocenyl-1,4-pentadien-3-one (**6**) proceeded at only a slow rate and gave a dark orange reaction mixture, the chromatographic separation of which on alumina gave 1-ferrocenyl-1-penten-3-one (**6a**) from the first fraction in an 18.1% yield and 1-ferrocenyl-3-pentanone (**6b**) from the second one in a 35.1% yield. There is some obscurity in the structural elucidation of **6** in terms of its IR spectrum, since the ethylenic absorption band at 1614 cm^{-1} was observed to be unusually stronger (ε'[*1]$=1740/2$) than the carbonyl absorption bands at 1649 ($\varepsilon'=416$) and 1665 cm^{-1}. However, the spectroscopic data of the reduction products, **6a** and **6b**, provided decisive evidence as to the cross-conjugated structure for the original ketone (**6**); that is, distinct carbonyl absorption bands were observed at 1660 and 1690 cm^{-1} for **6a**, and at 1710 cm^{-1} for **6b**.

The reduction of 2-(ferrocenylmethylene)cyclohexanone (**7**) afforded 2-(ferrocenylmethyl)cyclohexanone (**7a**), mp 75—77°C, in a 41% yield, whereas 2,6-di(ferrocenylmethylene)cyclohexanone (**8**) could not be hydrogenated under the conditions employed here, probably because of steric hindrance to the adsorption of the unsaturated system on the surface of the calalyst.

1,3-Diferrocenyl-2-buten-1-one (**1**) was slowly hydrogenated to the corresponding saturated ketone, 1,3-diferrocenyl-1-butanone (**1a**), in a 30% yield under the conditions shown in Table 1.

An interesting result was obtained with regard to the NMR signal of four methylene protons between the ferrocenyl and carbonyl groups in the reduction products, **3a**, **4a**, **5a**, **6a**, and **6b**. That is, these protons gave only one signal as a singlet peak in the τ 7.25—7.42 region, whereas the phenyl analogs, for example, 4-phenyl-2-butanone and 1,5-diphenyl-3-pentanone, gave the corresponding methylene signals as multiplet peaks[9] at τ 7.47 and 7.26, and at τ 7.63 and 7.26, respectively. The present observations suggest that the two methylenes between the ferrocenyl and carbonyl groups are equivalent in magnetic field. A similar observation, that [3]ferrocenophane gave only a singlet peak for its six methylene protons, has been presented by Rosenblum *et al.*, who interpreted their observation by assuming a rapid inversion of the bridged methylene groups.[10] Different alkyl groups on the carbonyl group do not cause any splitting of the signal, although the position of the signal is somewhat shifted. However, the corresponding aryl ketones, such as **9** and **10**, showed a multi-splitting of the methylene signal in their NMR spectra (see Table 2). The reason for the apparent magnetic equivalence of the four methylene protons in the ferrocenylethyl ketones (**3a**—**6b**) is not yet clear, but the following consideration may be pertinent. The chemical shift of the methyl protons of methylferrocene is found at τ 8.04,[11] while that of toluene is found at τ 7.66.[12] Thus, the deshielding effect exerted by a ferrocenyl group can be expected to be somewhat smaller than that by a phenyl group, and this might bring about an accidental coincidence of the chemical shifts of both methylene protons on α- and β-carbons to the carbonyl group. Moreover, the consideration may be extended to the possibility that some kind of participation of the iron atom of the ferrocene nucleus contributes to averaging the chemical shifts of these methylenes.

Ppt-Ni Catalyzed Reduction of β-Ferrocenyl-α,β-unsaturated Ketones. The effectiveness of ppt-Ni, which is prepared from an aqueous nickel chloride solution and zinc dust,[8] as a catalyst for the reduction of various unsaturated compounds has been demonstrated in previous papers.[6,7] Several β-ferrocenyl-α,β-unsaturated ketones were reduced by refluxing them with water in the presence of ppt-Ni. In this reaction water served as a hydrogen donor, and dioxane was used in order to keep the reaction mixture homogeneous. The results of these experiments are summarized in Table 3.

The reaction generally gave a reduction product, in an excellent yield, consisting of a mixture of a ketone and an alcohol. For example, 4-ferrocenyl-2-butanone (**3a**) and 4-ferrocenyl-2-butanol (**3b**) were obtained from 4-ferrocenyl-3-buten-2-one (**1**) in 10% and 90% yields respectively. The formation of alcohol as the main product suggests that the ppt-Ni-catalyzed reduction may be more drastic than the U-Ni-A-catalyzed one. The survival of the carbonyl group in the reduction of 1-ferrocenyl-5-methyl-1-hexen-3-one (**5**) may be attributed to the steric hindrance around it.

Relative Reactivity of β-Ferrocenyl-α,β-unsaturated Ketones and Related Compounds in

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[*1] $\varepsilon'=\frac{1}{cl}\log\frac{T_0}{T}$; c=concentration of **6**.

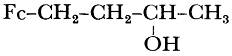
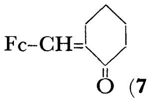
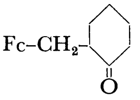
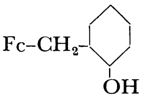
9) F. A. Bovey, "NMR Data Tables for Organic Compounds," Vol. I, John Wiley & Sons, N. Y. (1969), pp. 277, 440.

10) M. Rosenblum, A. K. Banerjee, N. Danieli, R. W. Fish and V. Schlatter, *J. Amer. Chem. Soc.*, **85**, 316 (1963).

11) Data in our laboratory.

12) Ref. 9, p. 169.

Table 3. Reduction of β-ferrocenyl-α,β-unsaturated ketones with water in the presence of ppt-Ni
Refluxing with 10 m*l* water and 5 m*l* dioxane; Reaction time 18 hr

Compound	(g)	ppt-Ni (g)*	Product	(%)
$Fc-CH=CH-CO-CH_3$ (**3**)	0.30	4.0	$Fc-CH_2-CH_2-CO-CH_3$ (**3a**)	10
			 $Fc-CH_2-CH_2-\underset{\mathrm{OH}}{\mathrm{CH}}-CH_3$ (**3b**)	90
$Fc-CH=CH-CO-CH_2-CH(CH_3)_2$ (**5**)	0.13	3.0	$Fc-CH_2-CH_2-CO-CH_2-CH(CH_3)_2$ (**5a**)	95
 (**7**)	0.32	4.0	 (**7a**)	25
			 (**7b**)	60
Fc-CH=CH-CO-CH=CH-Fc (**6**)	0.12	3.0	mixture $Fc-CH_2-CH_2-CO-CH_2-CH_2-Fc$ (**6b**) $Fc-CH_2-CH_2-CO-CH=CH-Fc$ (**6a**)	>80

* Every 10 g of ppt-Ni contains 1 g of nickel.

Catalytic Hydrogenation. It is known that the hydrogenation of an α,β-unsaturated carbonyl compound proceeds competitively through several reaction pathways, which involve either the 1,2- or the 1,4-addition of hydrogen.[13,14] The kinetic investigation of the hydrogenation of β-ferrocenyl-α,β-unsaturated ketones with U-Ni-A is expected to be useful for the elucidation of the reaction pathway, since U-Ni-A has been found to be particularly effective for the hydrogenation of ethylenic compounds over carbonyl compounds. The reaction rate was followed by measuring the hydrogen uptake. During the initial stage of the reaction, a linear relation holds between log $(H_\infty - H)$ and the reaction time (t) as a first-order reaction, where H_∞ is the total hydrogen uptake at the end point of the reaction and where H is the hydrogen uptake at each point of time. The slope of the straight line represents the initial rate constant (k) of the reaction. Thus, the initial rate constant in the first order (k) was calculated for each compound; these constants are listed in Table 4. The rate constants, obtained from the hydrogenation of several α,β-unsaturated ketones other than ferrocene derivatives under the same conditions as those employed in the ferrocene series, are listed in Table 5.

Table 4. Relative reactivity in hydrogenation of β-ferrocenyl-α,β-unsaturated ketones in the presence of U-Ni-A
Conc. 2.5×10^{-1} mol/*l*; U-Ni-A, 1.0 g; solvent, dioxane; shaking, 200 strokes/min

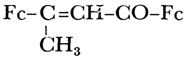
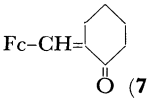
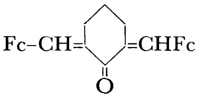
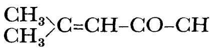
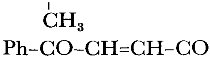
Compound	React. temp. (°C)	Rate const. k $(\mathrm{min}^{-1})\times10^{-2}$
$Fc-CH=CH-CO-CH_3$ (**3**)	17.2	5.76
	18.8	6.06
	22.4	6.72
	24.1	11.0
$Fc-CH=CHCO-C_2H_5$ (**4**)	26.1	6.45
$Fc-CH=CH-CO-CH_2-CH(CH_3)_2$ (**5**)	23.2	5.66
Fc-CH=CH-CO-CH=CH-Fc (**6**)	24.0	0.44
 $Fc-\underset{\mathrm{CH_3}}{\mathrm{C}}=CH-CO-Fc$ (**1**)	20.0	0.68
 (**7**)	23.0	2.02
 (**8**)	25.4	0.00

Table 5. Relative reactivity in hydrogenation of α,β-unsaturated ketones and related compound in the presence of U-Ni-A
2.5×10^{-1} mol/*l*; 200 strokes/min; solvent, dioxane; U-Ni-A, 1.0 g

Compound	React. temp. (°C)	Rate const. k $(\mathrm{min}^{-1})\times10^{-2}$
 $(CH_3)_2C=CH-CO-CH_3$ (**11**)	19.7	3.84
$Ph-CH=CH-CO-CH_3$ (**12**)	20.8	28.5
 $Ph-\underset{\mathrm{CH_3}}{\mathrm{C}}=CH-CO-Ph$ (**13**)	21.7	1.57
Ph-CO-CH=CH-CO-Ph (**14**)	21.9	8.40

Although the bulkiness of the ferrocenyl group had been expected to retard the reaction, the reaction rates of the hydrogenation of β-ferrocenyl-α,β-unsaturated ketones were found to be relatively high. This fact implies that the ferrocenyl group

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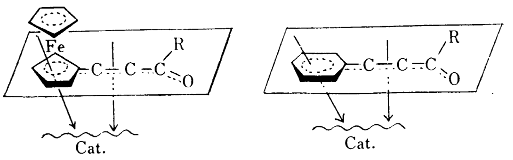
13) K. Hotta and T. Kubomatsu, The 21st Annual Meeting of the Chemical Society of Japan, Osaka, April, 1968, Proceeding Vol. I, p. 154.

14) F. J. McQuillin, W. O. Ord, and P. L. Simpson, *J. Chem. Soc.*, **1963**, 5996.

in the molecule approaches the surface of the catalyst with its less hindered side in the adsorbed transition state, as is shown sketchily in Fig. 1 (a).



(a) (b)

Fig. 1

Thus, the fact that 4-ferrocenyl-3-buten-2-one (**3**) was reduced easier than mesityl oxide (**11**) can be explained in terms of the cooperation of the ferrocenyl group. The larger rate constant of benzylideneacetone (**12**) can also be interpreted in the same manner. As is shown in Fig. 1 (b), the planar structure of the benzylideneacetone molecule may permit the facile adsorption of the conjugated system on the surface of the catalyst from either side of the molecule. On the other hand, the adsortpion of 4-ferrocenyl-3-buten-2-one (**3**) is permitted from only one side of the conjugated system, the other side being sterically hindered by a cyclopentadienyliron moiety. Hence, the reaction rate of the ferrocenyl compound (**3**) can naturally be expected to be considerably smaller than that of the phenyl analog.

Compounds with ferrocenyl groups at both ends of the molecule, such as **6** and **1**, were found to have far smaller reaction rates, as would be expected from the above-mentioned consideration. In the ferrocenylmethylene derivatives of cyclohexanone (**7** and **8**), the conjugated system is largely distorted from coplanarity. The steric environment retards the approach of the ethylenic bond to the surface of the catalyst, and results in a decrease in the rate constant. Especially, 2,6-di(ferrocenylmethylene)-cyclohexanone (**12**) could not be reduced under the conditions employed.

The steric effect of the alkyl groups on the carbonyl group was apparently not observed in this U-Ni-A catalyzed reaction, though it may be expected to affect the conformation of the ketone.[1] This fact implies that the coordination of the substrate molecule to the catalyst might occur preferentially on the part of the ferrocenyl and ethylenic groups.

The reaction pathways for the hydrogenation of β-ferrocenyl-α,β-unsaturated ketones can be considered to be as is shown in Scheme 1.[14]

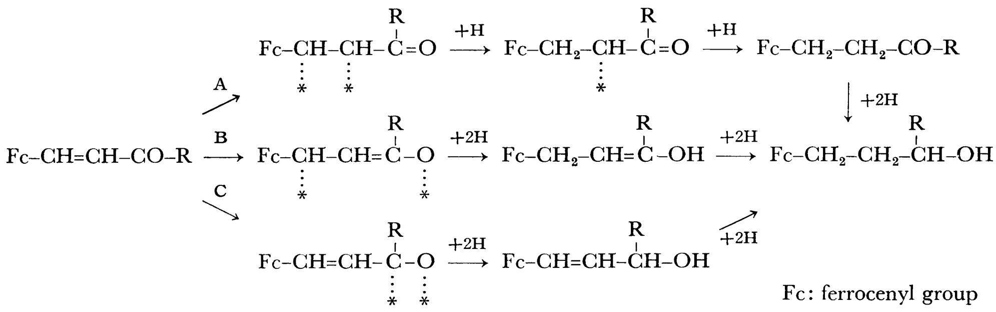
From the results mentioned above, it can be concluded that the path A, involving α,β-addition, is more favored than the others, while there may be some reaction by the path B at a higher reaction temperature, forming alcohol as a by-product. The path C, which may give an unsaturated alcohol, does not play any important role in this hydrogenation, for the reaction rate is not significantly affected by the nature of the alkyl substituent on the carbonyl group. On the other hand, the striking drops in the reaction rates of 1,3-diferrocenyl-2-buten-1-one (**1**) and the phenyl analog (**13**) clearly support the mechanism *via* the path A.

There is no evidence that any kind of electronic effect of the ferrocenyl group was operative in the reduction of these unsaturated ketones, though remarkable steric effects of the ferrocenyl group were observed.[7]

The electronic effects of the ferrocenyl group have been discussed by several authors,[15–17] especially the effect on the unusual stability of α-ferrocenylcarbonium ions. If such an anchimeric assistance by the *d*-orbital of the iron atom cooperates in the delocalization of the π-electron system of the α,β-unsaturated ketone, it would favor the coplanarity of the conjugated system including the ferrocenyl group, thus promoting the reaction *via* the path A.

Experimental

Materials. The β-ferrocenyl-α,β-unsaturated ketones



Fc: ferrocenyl group

Scheme 1. A schematic diagram of the hydrogenation pathways of β-ferrocenyl-α,β-unsaturated ketones.

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15) E. A. Hill and J. H. Richard, *J. Amer. Chem. Soc.*, **83**, 3840 (1961).

16) G. R. Buell, W. E. McEwen and J. Kleinberg, *ibid.*, **84**, 40 (1962).

17) T. G. Traylor and J. C. Ware, *ibid.*, **89**, 2304 (1967).

used in this study were synthesized according to the procedures reported in a preceding paper.[1)]

Catalyst. Ppt-Ni. Ppt-Ni was prepared by a procedure reported previously.[6)]

U-Ni-A. U-Ni-A was prepared from the ppt-Ni by digesting it with a 13% aqueous acetic acid solution, but the usual digestion procedure reported previously[8)] was somewhat modified as follows: 10 g of ppt-Ni was placed in a 200-m*l* Erlenmeyer flask, and then about 20 m*l* of 13% aqueous acetic acid solution was added all at once. With occasional shaking, the temperature of the solution was kept at about 30°C for several minutes; then 100 m*l* of the acetic acid was added in 20-m*l* portions over a period of about 20 min. After the evolution of gas had become gentle, the supernatant liquid was decanted away and the solid was washed several times with 50-m*l* portions of distilled water, methanol, and finally dioxane by decantation. Thus, 1 g of U-Ni-A was obtained.

General Procedure for Hydrogenation Using U-Ni-A. Freshly-prepared U-Ni-A (1 g) was placed, together with 10 m*l* of dioxane, in a hydrogenation vessel which was connected with a gas-buret containing hydrogen and stirred vigorously for about half an hour after the air in the vessel had been replaced with hydrogen. When the absorption of hydrogen by the catalyst ceased, a solution containing 5×10^{-3} mol of the respective unsaturated ketone in 10 m*l* of dioxane was introduced into the vessel. Then, the shaking was continued until the absorption of hydrogen in the buret became almost unrecognizable.[*2] At this time, the reaction was stopped and the reaction mixture was filtered. The solid on the filter was washed several times with methanol. The filtrate and the washings were then combined and dried over anhydrous magnesium sulfate. After the solvent had been removed under reduced pressure, a crude reaction product was purified by chromatography on alumina, using *n*-hexane except otherwise stated.

4-Ferrocenyl-2-butanone (3a). A yellow solid which had been obtained by chromatography was recrystallized from *n*-hexane to give yellow needles, mp 42—43°C,[*3] in about an 80% yield. IR (KBr disk): 3100, 2940, 1708, 1470, 1410, 1360, 1162, 1104, 1040, 1020, 999, and 816 cm^{-1}.

Found: C, 66.48; H, 5.54%. Calcd for $C_{14}H_{16}OFe$: C, 65.66; H, 6.25%.

1-Ferrocenyl-3-pentanone (4a). Yellow crystals; mp 51—52°C. IR (KBr disk): 3120, 2950, 1712, 1412, 1360, 1104, 1039, 1020, 998, and 817 cm^{-1}.

Found: C, 66.72; H, 6.50%. Calcd for $C_{15}H_{18}OFe$: C, 66.70; H, 6.67%.

1-Ferrocenyl-5-methyl-3-hexanone (5a). Yellow oil. IR (liq. film): 3110, 2950, 1710, 1467, 1408, 1367, 1288, 1224, 1102, 1070, 1039, 1020, 998, and 813 cm^{-1}.

Found: C, 68.27; H, 6.96%. Calcd for $C_{17}H_{22}OFe$: C, 68.49; H, 7.40%.

2-(Ferrocenylmethyl)cyclohexanone (7a). Yellow crystals; mp 75—77°C; 41% yield. IR (KBr disk): 3100, 2940, 2860, 1707, 1475, 1446, 1410, 1355, 1309, 1269, 1243, 1219, 1123, 1100, 1032, 1014, 994, 812, 749, and 670 cm^{-1}.

Found: C, 68.94; H, 6.39%. Calcd for $C_{17}H_{20}OFe$: C, 68.95; H, 6.78%.

1,5-Diferrocenyl-1-penten-3-one (6a) and 1,5-Diferrocenyl-3-pentanone (6b). A reddish-orange, oily product, which had been obtained by the reduction of 1,5-diferrocenyl-1,4-pentadien-3-one (**6**), was chromatographed on alumina using a mixture of benzene and *n*-hexane (1 : 1) as the solvent. 1,5-Diferrocenyl-3-pentanone (**6b**) was obtained from the first fraction as greenish-yellow needles, mp 110—111°C, in a 35% yield, while 1,5-diferrocenyl-1-penten-3-one (**6a**) was obtained from the second fraction as reddish-orange plates, mp 113—114°C, in an 18.1% yield. IR (KBr disk): (**6a**) $\nu_{C=O}$ 1660, 1690 cm^{-1}; $\nu_{C=C}$ 1604, 1621 cm^{-1}. (**6b**) $\nu_{C=O}$ 1710 cm^{-1}.

General Procedure for Hydrogenation Using Ppt-Ni. A solution of a given amount of unsaturated ketone (Table 3) in a mixture of dioxane (5 m*l*) and water (10 m*l*) was refluxed vigorously in the presence of 3.0—4.0 g of ppt-Ni for 18 hr. Then, the reaction mixture was filtered while hot, and the ppt-Ni on filter was washed several times with ether. The filtrate was extracted with ether. All the ethereal solutions were combined and dried over anhydrous magnesium sulfate. After the removal of the solvent, a yellowish-orange residue was chromatographed on alumina using a mixture of *n*-hexane and benzene (1 : 1) as the solvent to fractionate the products shown in Table 3.

4-Feffocenyl-2-butanol (3b). The crude mixture, obtained by the ppt-Ni-catalyzed reduction of 4-ferrocenyl-3-buten-2-one (**3**), was carefully chromatographed on deactivated alumina (100—200 mesh, exposed to air for 1.5 hr) in order to prevent such a reoxidation of the alcohol (**3b**) in the crude mixture to the ketone (**3a**) during alumina chromatography as was observed by Decombe *et al.*[18)] 4-Ferrocenyl-2-butanone (**3a**) was obtained in a 10% yield as the first fraction, using a mixture of *n*-hexane and benzene (1 : 1) as the solvent. After the ketone (**3a**) had been completely removed, elution with ether gave 4-ferrocenyl-2-butanol (**3b**) as red oil (90% yield). The structure of **3b** was established by means of its IR and NMR spectra. IR (liquid film): 3400 (OH), 3100, 2940, 1455, 1415, 1376, 1125, 1105, 1040, 1020, 998, 950, 925, and 812 cm^{-1}.

NMR (in $CDCl_3$): $Fc\text{-}\overset{1}{CH_2}\text{-}\overset{2}{CH_2}\text{-}\overset{3}{CH}(\overset{4}{OH})\text{-}\overset{5}{CH_3}$; τ 5.89 (5H, unsub. ring H, singlet), 5.93 (4H, sub. ring H, singlet), 6.15 (1H, H^3, multiplet), 7.56 (2H, H^1, multiplet), 8.39 (3H, H^2 and H^4, complex) and 8.83 (3H, H^5, doublet, $J=7$ Hz).

2-(Ferrocenylmethyl)cyclohexanol (7b). A dark brownish-red product, which had been obtained by the ppt-Ni-catalyzed reduction of 2-(ferrocenylmethylene)-cyclohexanone (**7**), was chromatographed on deactivated alumina using a mixture of *n*-hexane and benzene (1 : 1) as the solvent. 2-(Ferrocenylmethyl)cyclohexanone (**7a**) was obtained in a 25% yield from the first fraction. After the ketone (**7a**) had been completely removed, elution with ether afforded 2-(ferrocenylmethyl)cyclohexanol (**7b**) as a red oil in a 60% yield; this was identified by means of its IR spectra. IR (liquid film): 3430 (OH), 3100, 2940, 2870, 1450, 1104, 1038, 1018, 998, 972, 924, and 810 cm^{-1}.

[*2] When the hydrogenation was continued further, a very slow absorption of hydrogen was again observed due to the hydrogenation of the carbonyl group.

[*3] The melting point was observed to be somewhat lower than that previously reported (mp 45—46°C[18)]).

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18) J. Decombe, J. P. Ravoux and A. Dormont, *C. R. Acad. Sci., Paris, Ser. C*, **258**, 2348 (1964).