BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3273—3277 (1969)

β-Ferrocenyl-α,β-unsaturated Ketones. I. Condensation Reactions of Formylferrocene with Ketones

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(Received May 19, 1969)

The condensation reaction of formylferrocene with simple aliphatic and alicyclic ketones, as acetone, ethyl methyl ketone, isobutyl methyl ketone, and cyclohexanone, in the presence of piperidine as a condensing agent afforded seven kinds of β-ferrocenyl-α,β-unsaturated ketones. The geometric configurations of the unsaturated ketones were discussed on the basis of their NMR spectra, and the influences of the ferrocenyl group on the π-π^* transition bands in their UV spectra were also discussed.

It is widely known[1] that formylferrocene, like aromatic aldehydes, undergoes a variety of condensation reactions and thereby serves as an important starting material for the syntheses of many ferrocene derivatives. A Knoevenagel-type or aldol-type condensation[2] with a compound having a reactive methylene group under the influence of a base catalyst affords a ferrocene derivative with an unsaturated group conjugated with the ferrocene nucleus. Base-catalyzed condensations of formylferrocene or 1,1′-diformylferrocene with acetone have been reported by Boichard *et al.*[3] and by Osgerby and Pauson.[4] However, little has been reported on the condensation of formylferrocene with other simple aliphatic ketones.

A cyclic amine proved to be a very useful catalyst for the condensation of formylferrocene with nitroalkane.[5] In the present investigation, seven kinds of β-ferrocenyl-α,β-unsaturated ketones were prepared by the condensation of formylferrocene with various ketones, such as acetone, cyclohexanone, ethyl methyl ketone, and isobutyl methyl ketone, in the presence of piperidine, which was also found to be the most effective catalyst for such condensations.

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[1] M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Part 1, John Wiley & Sons, New York, N. Y. (1965), p. 80.

[2] G. D. Broadhead, J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.*, **1965**, 650; K. Schlögl, *Monatsh. Chem.*, **88**, 601 (1957); C. R. Hauser and J. K. Lindsey, *J. Org. Chem.*, **22**, 906 (1957); P. J. Graham, R. V. Lindsey, G. W. Parshal, M. L. Peterson and G. M. Whitman, *J. Am. Chem. Soc.*, **79**, 3416 (1957).

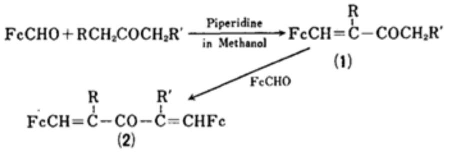
[3] J. Boichard, J. P. Monin and J. Tirouflet, *Bull. Soc. Chim. France*, **1963**, 851.

[4] J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.*, **1961**, 4604.

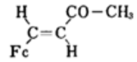
[5] M. Shiga, H. Kono, I. Motoyama and K. Hata, This Bulletin, **41**, 1897 (1968).

Results and Discussion

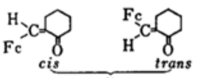
The α,β-unsaturated ketones obtained in the present study were five 1 : 1 adducts (from 1 mol of formylferrocene and 1 mol of ketone) (**1a**–**d**) and two 2 : 1 adducts (from 2 mol of the aldehyde and 1 mol of ketone) (**2a**,**b**).



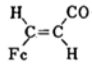
$$FcCHO + RCH_2COCH_2R' \xrightarrow[\text{in Methanol}]{\text{Piperidine}} FcCH{=}\overset{R}{C}{-}COCH_2R' \ (1) \xrightarrow{FcCHO} FcCH{=}\overset{R}{C}{-}CO{-}\overset{R'}{C}{=}CHFc \ (2)$$



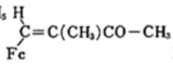
1a



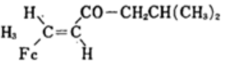
1b



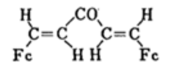
1c



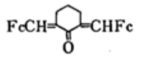
1c′



1d



2a



2b

$$FcCH{=}CHCOCH{=}CHFc \xrightarrow{H_2,\ U\text{-}Ni\text{-}A}$$

(**2a**)

$$FcCH_2CH_2COCH{=}CHFc + FcCH_2CH_2COCH_2CH_2Fc$$

(**3**) (**4**)

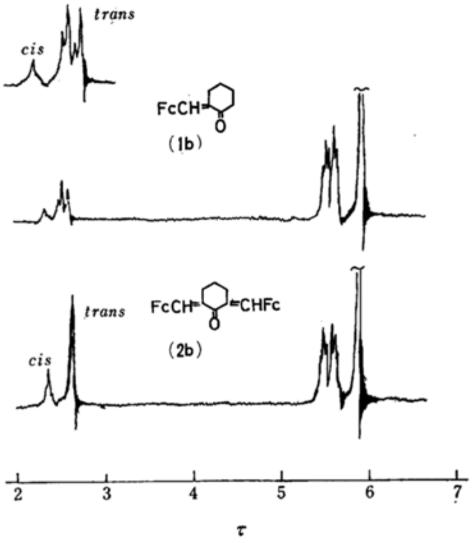


Fig. 1. NMR spectra of **1b** and **2b** in $CDCl_3$ (60 Mc).

The hydrogenation of 1,5-diferrocenyl-1,4-pentadien-3-one (**2a**) with Urushibara nickel A[6] proceeded step-by-step and afforded 1,5-diferrocenyl-1-penten-3-one (**3**) and 1,5-diferrocenyl-3-pentanone (**4**).

The NMR spectral data of the β-ferrocenyl-α,β-unsaturated ketones obtained here are listed in Table 1, together with those of vinylferrocene.

TABLE 1. THE NMR SPECTRA OF β-FERROCENYL-α,β-UNSATURATED KETONES AND VINYLFERROCENE (τ-value, in $CDCl_3$)

Compound	MP (°C)	Configuration	Cyclopentadienyl ring protons		Vinyl protons		Alkyl protons
			(unsubst.)	(subst.)	β	α	
$FcCH{=}CH_2$*			5.90(s)	5.80(t) 5.65(t)	3.48(q) (J=11, 17, 1.5 cps)	4.67(q) 4.97(q)	
1a	84—85	*trans*	5.84(s)	5.50(s)	2.56(d) (J=16 cps)	3.68(d)	7.73(s, CH_3)
1b	110—112	mixture (*trans*/*cis*=*ca.* 8)	5.87(s)	5.58(t) 5.48(t)	2.52(q, *trans*) (J=1.5 cps) 2.30(s, *cis*)		7.13—8.30 (broad, CH_2)
1c	101—102	*trans*	5.84(s)	5.52(s)	2.53(d) (J=16 cps)	3.66(d)	7.41(q, CH_2) 8.84(t, CH_3)
1d	31—32	*trans*	5.87(s)	5.52(s)	2.57(d) (J=16 cps)	3.68(d)	7.63(CH_2) 7.96(CH) 9.02(d, CH_3) (J=6.2 cps)
3	113—114	*trans*	5.85(s)	5.88(m) 5.52(s)	2.49(d) (J=16 cps)	3.65(d)	7.25 (s, CH_2CH_2)**
2a	203—204	*trans-trans*	5.85(s)	5.55(t) 5.45(t)	2.38(d) (J=15.5 cps)	3.43(d)	
2b	163—165	mixture	5.82(s)	5.56(t) 5.45(t)	2.59(s, *trans*) 2.33(s, *cis*)		7.26, 8.17 (broad CH_2)

* These data were in accord with those reported by Rausch *et al.*, (*J. Organometal. Chem.*, **11**, 317 (1968)).

** This signal did not show A_2B_2 type coupling.

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6) Y. Urushibara and S. Nishimura, This Bulletin, **28**, 466 (1955).

Table 2. The UV spectra data of β-ferrocenyl-α,β-unsaturated ketones* and other ferrocene derivatives**

Compound	Transition bands λ_{max} mμ (ε_{max})				
			π–π*	*d–d* type	
FcCH=CHCOCH$_3$ (**1a**)	210 (15900)	258 (9860)	305 (14300)	369 (2150)	486 (1750)
FcCH=CHCOC$_2$H$_5$ (**1c**)	211 (26150)	258 (9500)	305 (24400)	371 (1950)	486 (1600)
FcCH=C(CH$_3$)COCH$_3$ (**1c′**)	218 (6386)	256 (4959)	308 (5710)	357 (1277)	479 (864)
FcCH=CHCOCH=CHFc (**2a**)	207 (35940)	—	340 (17870)	402 (4140)	527 (5080)
FcCH=CHCOC$_6$H$_5$**				387 (3120)	490 (2970)
FcCOCH=CHC$_6$H$_5$**				383 (1960)	484 (1660)

* Ethanol was used as solvent.

** R.T. Lundiquist and M. Cais, *J. Org. Chem.*, **27**, 1167 (1962).

Representative NMR spectra of **1b** and **2b** are shown in Fig. 1. The UV spectra of some of these unsaturated ketones are listed in Table 2, together with those of the related compounds.

When symmetrical ketones, such as acetone and cyclohexanone, were employed, considerable quantities of 2 : 1 adducts (**2a** and **2b**) were obtained as by-products besides the 1 : 1 adducts (**1a** and **1b**). On the other hand, unsymmetrical ketones, such as ethyl methyl ketone and isobutyl methyl ketone, gave 1 : 1 adducts (**1c**, **1c′**, and **1d**) exclusively.

A well-known reaction of this type is the Claisen-Schmidt condensation[7] with aromatic aldehydes. Benzaldehyde condenses with acetone under acidic conditions to form dibenzylideneacetone predominantly, whereas under basic conditions the main product is benzylideneacetone, accompanied by dibenzylideneacetone as a minor product.

It is known that ethyl methyl ketone suffers an enolization-controlled reaction mainly on the methyl side rather than on the ethyl side under basic conditions.[8] The same tendency was observed in the present experiments. Ethyl methyl ketone condensed with formylferrocene to afford **1c** as the main product and **1c′** as a minor product, while isobutyl methyl ketone afforded **1d** as the sole product. These observations indicate that steric hindrance against an electrophilic attack on the α-carbon to the carbonyl group of the ketone is apparently an important factor in the orientation of these condensation reactions.

Assignment of the Geometrical Configuration of the α,β-Unsaturated Ketone. The geometrical configurations of the α,β-unsaturated ketones were determined in terms of the coupling constants between the vinyl protons. As is shown in Table 1, α- and β-protons of the vinyl group gave respective doublet peaks, corresponding to an AB pattern. The coupling constant of the vinyl protons was 16 cps in the cases of **1a**, **1c**, and **1d**, and 15.5 cps for **2a**. The magnitude of the coupling constant reveals these α,β-unsaturated ketones to have trans configurations, in which ferrocenyl and carbonyl groups are on opposite sides of the double bond.[9] In this connection, it has been pointed out that the coupling constant of trans vinyl protons is 17 cps for vinylferrocene itself and 12.5 cps for *trans*-1-ferrocenyl-2-nitroethylene.[5]

The compound **1b** gave complex signals due to the β-vinyl proton in the range from τ 2.26 to 2.60, as is shown in Fig. 1. In the trans isomer of this compound, in which the ferrocenyl group is on the side opposite to that of the carbonyl group, a signal of the vinyl proton is expected to appear in a higher field, because of an anisotropic effect of the carbonyl group on the same side, than that of the cis isomer. Further, the splitting of the former is expected, considering a long-range coupling with a methylene group situated trans to the vinyl proton. Therefore, a quartet in the higher field, centered at about τ 2.52, was assigned to the vinyl proton of the trans isomer, whereas a broad signal centered at about τ 2.30 was assigned to that of the cis isomer. On the basis of the relative intensities of these signals, the trans : cis ratio in **1b** was determined to be about 8 : 1.

The compound **2b**, which contains two exo-double bonds in the molecule, showed the signals of the vinyl protons at τ 2.59 and 2.33 as two singlets. The former, in the higher field, was assigned to the trans vinyl proton for the same reason as has been described for **1b**, and the latter was assigned to the cis. No such long-range coupling as was observed in *trans*-**1b** was observed in *trans*-**2b**, probably because of a conformational change in the cyclohexanone ring caused by the two exo-double bonds.

Ultraviolet Spectra. The UV spectra of **1a**, **1c**, **1c′**, and **2a** were observed in 95% ethanol and

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[7] L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Reinhold Pub. Co., New York, N. Y. (1961), p. 467.

[8] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Company, New York, N. Y. (1959), p. 383.

[9] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London (1959), p. 85.

are summarized in Table 2, together with those of some related ferrocene derivatives. The strongest absorption bands, at 305—308 mμ, in the spectra of **1a**, **1c**, and **1c′** can be assigned to the π–π^* transition band of the α,β-unsaturated ketone conjugated with the ferrocene nucleus, while the corresponding absorption bands of nitroalkenylferrocenes appear at about 325 mμ.[10] As the π–π^* transition band of methyl vinyl ketone has been reported to appear at 219 mμ (ε=3600),[11] the replacement of a vinyl hydrogen by a ferrocenyl group causes a remarkable shift of this band to a longer wavelength (305 mμ). Such a large bathochromic shift (85 mμ) by a ferrocenyl group has also been observed in the nitroalkene series.[10]

The UV spectrum of ferrocene has been discussed in detail by Scott and Becker,[12] who assigned the two long wavelength bands at 325 and 440 mμ to *d–d* type transitions, with some mixing with ring orbitals. In the cases of **1a**, **1c**, and **1c′**, both of these long wavelength bands, due to the *d–d* type transitions, appeared in the longer-wavelength region, namely, at about 370 and 480 mμ respectively.

In the spectrum of **2a**, the π–π^* and *d–d* type transition bands exhibited larger bathochromic shifts and appeared at 340, 402, and 527 mμ respectively.

However, such a large bathochromic shift as that observed in the π–π^* transition band cannot simply be explained in terms of conjugation of the α,β-unsaturated ketone with the ferrocene ring. It will be necessary to consider the interaction of the non-bonding *d*-orbitals of the metal in the ferrocene nucleus with the π-orbital of the side chain on the ferrocene ring.

Further work on this subject is now in progress, and a more detailed discussion will be presented in the near future.

Experimental

General Procedure for the Preparation of β-Ferrocenyl-α,β-unsaturated Ketones. A solution of formylferrocene (1 mol) and a ketone (2 mol) in methanol was left to stand for 2—4 days in the presence of piperidine (2 mol) at room temperature. After the subsequent removal of the solvent under reduced pressure, a deep red residue was dissolved in benzene; then the benzene solution was washed repeatedly with water and dried over anhydrous magnesium sulfate. The benzene solution was concentrated under reduced pressure and then chromatographed on alumina using a mixture of benzene-hexane (1 : 1) as a sovlent. The isolated products were identified by means of the NMR, IR, and UV spectra and elemental analyses.

4-Ferrocenyl-3-buten-2-one (1a) and 1,5-Diferrocenyl-1,4-pentadien-3-one (2a). The condensation product from the reaction of formylferrocene and acetone was chromatographed on alumina. The first fraction gave **1a** in a 78.9% yield. The product was recrystallized from petroleum ether to afford a deep red powder, mp 84—85°C (lit mp 86°C[3]). IR (in CCl_4): 3100, 1689, 1666, 1619, 1601, 1359, 1251, 1186, 1108, 1043, 1028, 998 and 964 cm^{-1}.

Found: C, 67.25; H, 5.70%. Calcd for $C_{14}H_{14}OFe$: C, 66.18; H, 5.52%.

The second fraction gave **2a** in a 4.3% yield; it was recrystallized from benzene-hexane (1 : 1) to afford reddish-orange leaflets, mp 203—204°C. IR (in CCl_4): 3100, 1665, 1649, 1614, 1104, 1090, 1037, 1024 and 995 cm^{-1}.

Found: C, 65.89; H, 4.81%. Calcd for $C_{25}H_{22}OFe_2$: C, 66.71; H, 4.89%.

2-(Ferrocenylmethylene)cyclohexanone (1b) and 2,6-Bis(ferrocenylmethylene)cyclohexanone (2b). The condensation product from formylferrocene and cyclohexanone was chromatographed on alumina. From the first fraction, **1b** was obtained, on recrystallization from benzene-hexane (1 : 1), as deep red powder, mp 110—112°C, in a 70.4% yield. IR (in CCl_4): 3080, 2920, 1677, 1585, 1309, 1239, 1137, 1100, 1040 and 991 cm^{-1}.

Found: C, 69.79; H, 6.16%. Calcd for $C_{17}H_{18}OFe$: C, 69.35; 6.11%.

The second fraction gave **2b**; it was then recrystallized from petroleum ether-benzene (1 : 1) to give deep red needles, mp 163—165°C, in a 12% yield. IR (in CCl_4): 3100, 2940, 1666, 1604, 1304, 1273, 1240, 1158, 1136, 1101, 1037 and 991 cm^{-1}.

Found: C, 69.20; H, 5.55%. Calcd for $C_{28}H_{26}OFe_2$: C, 68.60; H, 5.30%.

1-Ferrocenyl-1-penten-3-one (1c) and 4-Ferrocenyl-3-methyl-3-buten-2-one (1c′). 1-Ferrocenyl-1-penten-3-one (**1c**) was obtained as a first fraction from the chromatographic separation of the crude product, which had been obtained by the reaction of formylferrocene and ethyl methyl ketone. The recrystallization of **1c** from petroleum ether gave a deep red powder, mp 101—102°C, in a 41.2% yield. IR (in CCl_4): 3100, 2900, 1688, 1665, 1621, 1606, 1350, 1100 and 1025 cm^{-1}.

Found: C, 68.00; H, 6.20%. Calcd for $C_{15}H_{16}OFe$: C, 67.20; H, 5.95%.

A small amount of another product was isolated from the second fraction as reddish-orange needles, mp 162—164°C. It was found to be 4-ferrocenyl-3-methyl-3-buten-2-one (**1c′**) by means of a study of the IR, UV, and NMR spectra and by elemental analysis. IR (in CCl_4): 3110, 2900, 1682, 1658, 1604, 1107, 1038 and 1000 cm^{-1}. NMR (in $CDCl_3$): τ 8.45—8.80 (methyl), 5.82 (unsubstituted ring), 5.40—5.60 (substituted ring) and 2.53 (vinyl).

Found: C, 67.83; H, 6.64%. Calcd for $C_{15}H_{16}OFe$: C, 67.20; H, 5.95%.

1-Ferrocenyl-5-methyl-1-hexen-3-one (1d). The repeated chromatographic purification of the crude product from isobutyl methyl ketone afforded **1d**. Recrystallization from *n*-hexane gave reddish orange needles, mp 31—32°C, in a 54.2% yield. IR (in CCl_4):

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[10] Unpublished data.

[11] L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, **1941**, 815.

[12] D. R. Scott and R. S. Becker, *J. Chem. Phys.*, **35**, 516, 2246 (1962); D. R. Scott and R. S. Becker, *J. Organometal. Chem.*, **4**, 409 (1965).

3140, 2950, 2800, 1685, 1656, 1619, 1602, 1472, 1363, 1290, 1170, 1109, 1058, 1040, 997 and 960 cm^{-1}.

Found: C, 69.00; H, 7.04%. Calcd for $C_{17}H_{20}OFe$: C, 68.96; H, 6.76%.

Catalytic Hydrogenation of 1,5-Diferrocenyl-1,4-pentadien-3-one (2a). Dienone **2a** (1.1 g) dissolved in 10 m*l* of dioxane was placed in a hydrogenating vessel together with 0.5 g of Urushibara nickel A and vigorously shaken with hydrogen for 7 hr at atmospheric pressure and at 24°C. After the catalyst had been removed by filtration, the filtrate was poured into water; the aqueous layer thus obtained was extracted with ether. The extract was washed with water and dried over anhydrous magnesium sulfate. The removal of the solvent under reduced pressure gave 1.2 g of a red oil; this oil was then subjected to chromatographic separation on alumina using benzene - hexane (1 : 1). The first fraction afforded 0.4 g of a yellow solid which was recrystallized from *n*-hexane to give 1,5-diferrocenyl-3-pentanone (**4**) as greenish-yellow needles, mp 110—111°C. IR (in CCl_4): 3100, 2900, 1710, 1475, 1440, 1413, 1362, 1110, 1090, 1043, 1027 and 1003 cm^{-1}. NMR (in $CDCl_3$): τ 7.39 (methylene), 5.94 (substituted ring), 5.89 (unsubstituted ring).

Found: C, 65.62; H, 5.44%. Calcd for $C_{25}H_{26}OFe_2$: C, 66.12; H, 5.73%.

From the second fraction, 0.2 g of a solid was obtained. Recrystallization from benzene afforded 1,5-diferrocenyl-1-penten-3-one (**3**) as reddish-orange plates, mp 113—114°C. IR (in CCl_4): 3100, 1690, 1660, 1621, 1604, 1355, 1215, 1180, 1107, 1093, 1045, 1030 and 1000 cm^{-1}.

Found: C, 66.02; H, 5.30%. Calcd for $C_{25}H_{24}OFe_2$: C, 66.41; H, 5.31%.

The authors wish to express their thanks to Professor Michio Kobayashi, Tokyo Metropolitan University, for his kind advice regarding the identification of the geometrical configuration. Thanks are also due to Mr. Kisaburo Yamazaki and his group of the Central Research Laboratory, Yamanouchi Pharmaceutical Co., Ltd., for the measurement of the NMR spectra and to Mr. Takeo Akiyama, Sophia University, for the measurement of the UV spectra.