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β-Ferrocenyl-α,β-unsaturated Ketones. III.[1] The Conformational Study of β-Ferrocenyl-α,β-unsaturated Ketones by Means of IR Spectroscopy

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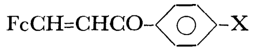
The geometrical and conformational isomerism of various β-ferrocenyl-α,β-unsaturated ketones, most of which had been reported in a previous paper, was discussed on the basis of their IR spectra in the 1700—1600 cm^{-1} range and their NMR spectra. An unusually strong IR absorption of the olefinic double bond was observed in comparison with that of the carbonyl group. Considering the IR and NMR data, it was concluded that 3-ferrocenyl-1-(p-substituted phenyl)-2-propen-1-ones may mostly exist in a *s-cis* conformation.

Generally, α,β-unsaturated ketones may exist in *s-cis* and *s-trans* forms. For the conformational study of such unsaturated ketones, UV and IR spectroscopic methods are very useful and a number of spectroscopic data concerning α,β-unsaturated carbonyl compounds have been reported.[2–5] Recently, Dimmock and his co-workers reported on their observation of carbonyl absorption bands due to *s-cis* and *s-trans* isomerism in the IR spectra of substituted 1-phenyl-1-hepten-3-ones and related compounds.[6] However, in such aryl-substituted α,β-unsaturated carbonyl compounds, the absorption bands near 1600 cm^{-1} due to the conjugated C=C stretching vibrations overlap unfavorably with the bands due to the C=C skeletal in-plane vibrations of the aromatic ring. On the other hand, the IR spectra of β-ferrocenyl-α,β-unsaturated ketones show a distinct absorption band due to the C=C bond conjugated with the ferrocenyl group, since the ferrocenyl group has no appreciable absorption in this region. Hence, they seem to be compounds favorable for such conformational study.

FcCH=CHCOR

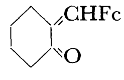
(**1**)

1a: R=CH_3
1b: R=C_2H_5
1c: R=$CH_2CH(CH_3)_2$
1d: R=$C(CH_3)_3$



(**2**)

2a: X=H
2b: X=CH_3
2c: X=OCH_3
2d: X=Cl
2e: X=NO_2



(**1e**)

FcCH=CHCOCH=CHFc

(**3**)

In this investigation, the IR spectra of five β-ferrocenyl-α,β-unsaturated ketones (**1**), which had been reported in a preceding paper,[7] and those of five 3-ferrocenyl-1-(p-substituted phenyl)-2-propen-1-ones (**2**) were measured in carbon tetrachloride, and the assignment of bands near 1600 cm^{-1} to *s-cis* and *s-trans* isomers was discussed.

Results

The IR spectrum of 4-ferrocenyl-3-buten-2-one (**1a**) in a KBr disk shows two strong bands, at 1655 and 1619 cm^{-1}, due to the carbonyl and ethylenic stretching vibrations respectively. When it was observed in solution, a new band appeared near these bands, although its position and intensity varied with the nature of the solvent employed, as is shown in Fig. 1. These phenomena, also observed in all the other compounds studied here except **1e**, may be attributed to the presence of two rotational isomers, *s-cis* and *s-trans*, in the solution.

Table 1 summarizes the absorption maxima, ν_{max} and the extinction coefficients, ε' (for the definition of ε', see the Experimental part), of these bands, measured in CCl_4. According to the conformational study by Erskine and Waight[2] using α,β-unsaturated ketones which maintain their rigid conformations, the carbonyl stretching bands appear in the 1704—1684 cm^{-1} range (ε 250—333) for *s-cis* and the 1679—1669 cm^{-1} (ε 454—670) for *s-trans* isomers, while the ethylenic stretching bands

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[1] Part II: H. Kono, M. Ishige, K. Sakai, M. Shiga, I. Motoyama and K. Hata, This Bulletin **43**, 867 (1970).

[2] R. L. Erskine and E. S. Waight, *J. Chem. Soc.*, **1960**, 3425.

[3] R. D. Campbell and N. H. Cromwell, *J. Amer. Chem. Soc.*, **79**, 3456 (1957).

[4] N. H. Cromwell and R. P. Cahoy, *ibid.*, **80**, 5524 (1958).

[5] M. E. Kronenberg and E. Havinga, *Rec. Trav. Chim. Pays-Bas*, **84**, 17 (1965).

[6] J. R. Dimmock, P. L. Carter and P. D. Ralph, *J. Chem. Soc., B*, **1968**, 698.

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

TABLE 1. THE IR SPECTRA DATA OF β-FERROCENYL-α,β-UNSATURATED KETONES (in CCl_4)

Compound	Concentration (mol/*l*) 10^{-2}		ν_{max}(cm^{-1}) s-*cis* C=O(ε')[b]	s-*cis* C=C(ε')	s-*trans* C=O(ε')	s-*trans* C=C(ε')
1a	1.654		1684(171)	1597(578)	1665(438)	1615(308)
1b	1.665		1688(218)	1604(568)	1663(246)	1621(216)
1c	1.442		1686(190)	1601(572)	1653(167)	1619(244)
1d			1685(0.717[c])	1600(0.164[c])	1663(0.095[c])	1617(0.248[c])
1e	1.527	*trans*[a]	1676(259)	1584(369)	—	—
		cis[a]	1684(sh)	1600(sh)	—	—
2a	1.285		1661(446)		1635(127)	
2b	1.813		1659(548)		1636(110)	
2c	1.365		1656(532)		—	
2d	1.073		1658(495)		1640(118)	
2e			1647		—	

Compound	$\Delta\nu_{max}$(cm^{-1}) (s-*cis*~s-*trans*) C=O	(s-*cis*~s-*trans*) C=C	(C=O~C=C) s-*cis*	(C=O~C=C) s-*trans*	$\varepsilon'_{s\text{-}cis}/\varepsilon'_{s\text{-}trans}$ C=O	$\varepsilon'_{s\text{-}cis}/\varepsilon'_{s\text{-}trans}$ C=C	$\varepsilon'_{C=O}/\varepsilon'_{C=C}$ s-*cis*	$\varepsilon'_{C=O}/\varepsilon'_{C=C}$ s-*trans*
1a	19	18	87	50	0.39	1.88	0.30	1.42
1b	25	17	84	42	0.89	2.63	0.38	1.14
1c	23	18	87	34	1.14	2.34	0.33	0.68
1d	22	17	85	46	2.38[d]	2.60[d]	2.89	1.72
1e	—	—	92					
	—	—	84					
2a	26				3.51			
2b	23				4.21			
2c	—							
2d	18				4.96			
2e	—							

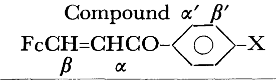
[a] Configuration with respect to C=C double bond.

[b] Definition of ε': see Experimental part.

[c] Absorbance $\log_{10} T_0/T$.

[d] Calculated from absorbance values of *s-cis* and *s-trans* isomers.

TABLE 2. THE NMR SPECTRA OF 3-FERROCENYL-1-(*p*-SUBSTITUTED PHENYL)-2-PROPEN-1-ONE (**2**)
(τ-value, in $CDCl_3$)

Compound 		Cyclopentadienyl ring protons (Unsubst.)	Cyclopentadienyl ring protons (Subst.)	Vinyl protons α	Vinyl protons β	Benzene ring protons β'	Benzene ring protons α'
2a	X=H	5.84(s)	5.55(t) 5.42(t) (J=2 Hz)	2.88(d)	2.23(d)	2.44(m)	1.98(m)
				($J_{\alpha\beta}$=15 Hz)			
2b	X=CH_3*	5.85(s)	5.54(t) 5.42(t) (J=2 Hz)	2.91(d)	2.23(d)	2.71(d)	2.08(d)
				($J_{\alpha\beta}$=15 Hz)		($J_{\alpha'\beta'}$=8 Hz)	
2c	X=OCH_3**	5.87(s)	5.56(t) 5.43(t) (J=2 Hz)	2.89(d)	2.24(d)	3.05(d)	1.99(d)
				($J_{\alpha\beta}$=15 Hz)		($J_{\alpha'\beta'}$=9 Hz)	
2d	X=Cl	5.84(s)	5.52(t) 5.42(t) (J=2 Hz)	2.95(d)	2.22(d)	2.55(d)	2.07(d)
				($J_{\alpha\beta}$=15 Hz)		($J_{\alpha'\beta'}$=9 Hz)	
2e	X=NO_2	5.83(s)	5.44 (broad)	2.97(d)	2.17(d)	1.64(d)	1.93(d)
				($J_{\alpha\beta}$=15 Hz)		($J_{\alpha'\beta'}$=9 Hz)	

* τ 7.58(s) ** τ 6.16

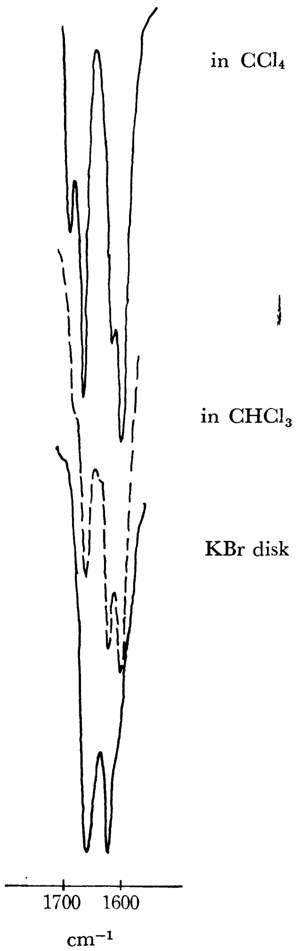


Fig. 1. IR spectra of 4-ferrocenyl-3-buten-2-one (**1a**) in various media.

are in the 1633—1613 cm^{-1} range for the *s-cis* and the 1639—1615 cm^{-1} range for the *s-trans* isomers. Following their observation, the carbonyl band with the higher frequency and the olefinic band with the lower frequency were identified as being due to *s-cis*, and the another pair were identified as being due to the *s-trans* isomer. Table 1 shows that the carbonyl bands for *s-cis* isomers are generally 19—25 cm^{-1} higher than those for *s-trans*, while the olefinic bands for *s-cis* isomers are 17—18 cm^{-1} lower than those for *s-trans*. The differences between the absorption maxima of the carbonyl and the olefinic bands were found to be 84—87 cm^{-1} and 34—50 cm^{-1} for *s-cis* and *s-trans* isomers respectively. These values are in accord with the observations of Braude and his co-workers.[8]

In the IR spectrum of 2-(ferrocenylmethylene)-cyclohexanone (**1e**), four bands were also observed in this region, in spite of its exclusive *s-cis* structure. This can, however, be explained by the presence of the geometric isomers with respect to the olefinic double bond. The bands at 1676 and 1584 cm^{-1} were assigned to the isomer in which ferrocenyl group lies *trans* to the carbonyl group, while those at 1684 and 1600 cm^{-1}, with lower intensities, were assigned to the *cis* isomer.

3-Ferrocenyl-1-(*p*-substituted phenyl)-2-propen-1-ones (**2**) were prepared by the base-catalyzed condensation[9] of formylferrocene with *p*-substituted acetophenones. It was proved, by means of their NMR spectra (Table 2), that their olefinic double bonds had *trans* configurations, as had previously been shown in the case of 4-ferrocenyl-3-buten-2-one and related compounds.[7]

In the IR spectra of the aryl ketones (**2**), the strong absorptions due to the carbonyl group of sterically-favored *s-cis* isomers appeared at about 1660 cm^{-1}, about 20 cm^{-1} lower than those of the corresponding alkyl ketones (**1**). In addition to the strong bands, weak bands were observed in the 1640—1635 cm^{-1} range in the spectra of **2a**, **2b**, and **2d**, the corresponding bands being absent in those of **2c** and **2e**. These bands are considered to be due to the carbonyl group of *s-trans* isomers. On the other hand, the band with several shoulders at about 1600 cm^{-1} could not be assigned because of the heavy overlapping of the olefinic band with the aromatic band.

Discussion

The main factors influencing the conformation of α,β-unsaturated ketones are the steric environment around the carbonyl group, especially the steric requirements of the substituent, and the nature of the solvent. It can be seen in Table 1 that the alteration of an alkyl group on the carbonyl group has a great influence on the extinction coefficients of both carbonyl and ethylenic absorption bands, whereas it does not very much affect the frequencies of these bands. The ratios of the extinction coefficient, $\varepsilon'_{C=O}/\varepsilon'_{C=C}$, were calculated to be 0.30—2.89 for *s-cis* isomers and 0.68—1.72 for *s-trans* isomers. These values are unusually small compared with those of the ordinary α,β-unsaturated ketones previously reported: $\varepsilon_{C=O}/\varepsilon_{C=C}$ for *s-cis*: 0.7—2.5; $\varepsilon_{C=O}/\varepsilon_{C=C}$ for *s-trans*: 6—9.[2] It is thus noticeable that the olefinic double bond in β-ferrocenyl-α,β-unsaturated ketones has an unusually strong absorption in this region. The enhanced olefinic absorption may be due to the conjugation of the double bond with the ferrocenyl group, a conjugation originating in the great electron-releasing ability of the ferrocenyl nucleus. In this connection, it must be mentioned that the ethylenic band of 1,5-diferrocenyl-1,4-pentadien-3-one (**3**) at

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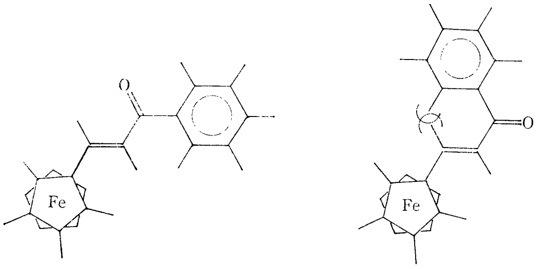
8) E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, **1955**, 3766.

9) C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 906 (1957).

1614 cm^{-1} was observed to be unusually stronger ($\varepsilon'=1740/2$) than the carbonyl band at 1649 cm^{-1} ($\varepsilon'=416$).[1)]

The examination of the molecular structure of the *s-trans* conformation suggests that a bulky group on the carbonyl group may force the conjugated system of the unsaturated ketone out of coplanarity or force it to take the *s-cis* conformation. Although the estimation of the isomer ratio is impossible from the spectra data shown in Table 1, it is clear that the concentration of the *s-trans* isomer qualitatively decreases with an increase in the bulkiness of the alkyl group on the carbonyl group. The steric situation is especially emphasized in aryl ketones (**2**). An aryl substituent on the carbonyl group brings about a great decrease in the concentration of the *s-trans* isomer. If the whole conjugated system of the aryl-substituted unsaturated ketone with an *s-trans* conformation takes a coplanar arrangement, the ortho hydrogen atom of the phenyl group may overlap heavily with the β-vinyl hydrogen, as is shown in Fig. 2. Thus, the *s-cis* isomer, which is free from this strain and which may be somewhat stabilized by holding the whole conjugated system of the molecule in a coplanar conformation, will be predominant in solution. This consideration is consistent with the observations that the $\varepsilon'_{s\text{-}cis}/\varepsilon'_{s\text{-}trans}$ ratios of carbonyl bands in the IR spectra of the aryl ketones (**2**) exhibited considerably larger values than those of the alkyl ketones (**1**), and that the chemical shift of the β-vinyl proton of the aryl ketones (**2**) appeared in a low field, as is shown in Table 2, probably due to the anisotropic effect of the carbonyl group.



s-cis *s-trans*

Fig. 2.

The nature of the solvent used for the measurement will also affect the population of the isomers. In a polar solvent, solvation will take place so as to keep the positive and negative centers in the molecule very far apart from each other. Thus, *s-trans* would be a more favorable conformation than *s-cis* in a polar solvent. If the delocalization of the positive charge extended to the ferrocene ring because of the electron-releasing character of the ferrocene nucleus, the predominance of the *s-trans* conformation would be more promoted. However, contrary to expectation, no appreciable solvent effect was observed, probably because the steric effect overcomes the solvent effect.

Supposing a cyclopentadienyl ring in the ferrocene nucleus lies on a plane of the side-chain olefinic double bond, the other part of a ferrocene molecule stands out of this plane and the iron atom is situated so close to the π-orbital of the side chain that a certain anchimeric effect between them may be expected. Therefore, the conjugation of the π-electron system in the side chain with the ferrocene ring in β-ferrocenyl-α,β-unsaturated ketones may be somewhat different in nature from that with the benzene ring in β-phenyl analogs. Thus, such an anchimeric effect might contribute to some extent to the enhanced population of the *s-cis* isomer in β-ferrocenyl-α,β-unsaturated ketones, in addition to the prevailing steric effect.

Experimental

Spectral Measurements. The infrared spectra were measured in carbon tetrachloride with a Hitachi EPI-G2 grating spectrometer, using a rock salt cell 0.052 cm thick. The extinction coefficient, ε', employed in this study is defined as follows:

$$\varepsilon^{a}_{s\text{-}cis} = \frac{\log T_0/T_{s\text{-}cis}}{x_{s\text{-}cis}\cdot c\cdot l} = \frac{\varepsilon'_{s\text{-}cis}}{x_{s\text{-}cis}}$$

$$\varepsilon^{a}_{s\text{-}trans} = \frac{\log T_0/T_{s\text{-}trans}}{(1-x_{s\text{-}cis})\cdot c\cdot l} = \frac{\varepsilon'_{s\text{-}trans}}{1-x_{s\text{-}cis}}$$

where ε^{a} is a molar extinction coefficient, $x_{s\text{-}cis}$ is the molar ratio of the *s-cis* isomer, *c* is the molar concentration of the solution measured, *l* is the path length in cm, and T_0/T is the peak optical density.

The absorbances ($\log_{10} T_0/T$) of both the C=O and C=C absorption peaks were found to have a good linear relationship with the molar concentration of the unsaturated ketone.

The NMR spectra of **2** were measured in $CDCl_3$ with a Hitachi model H-60 spectrometer.

Materials: 4-Ferrocenyl-2-buten-2-one (**1a**), 1-ferrocenyl-1-penten-3-one (**1b**), 1-ferrocenyl-5-methyl-1-hexen-3-one (**1c**), 1-ferrocenyl-4,4-dimethyl-1-penten-3-one (**1d**), and 2-(ferrocenylmethylene)cyclohexanone (**1e**) were each prepared by the base-catalyzed condensation of formylferrocene with the corresponding ketones by means of a procedure reported previously.[7)]

1-Ferrocenyl-4,4-dimethyl-1-penten-3-one (1d). Attempts at the chromatographic purification of **1d** were unsuccessful because it easily decomposed on alumina to give formylferrocene and pinacolone. When the crude material was left standing for several months, a small amount of long, dark red needles grew out of the crude solid. When collected, this was proved to be a pure substance by its sharp mp 91—92°C. It was identified as **1d** by means of its IR and UV spectra. λ_{max} (95% ethanol) 225, 260, 305, *ca.* 364(sh), and 480 mμ.

3-Ferrocenyl-1-(*p*-substituted phenyl)-2-propen-1-ones (2). These substances were prepared by the condensation of formylferrocene with *p*-substituted acetophenone in the manner used to prepare 3-ferrocenyl-1-phenyl-2-propen-1-one by Hauser and Lindsay.[9)]

3-Ferrocenyl-1-phenyl-2-propen-1-one (2a). The crude product obtained by the condensation of formylferrocene and acetophenone was recrystallized from ethanol to afford violet needles; mp 142—145°C (lit.,[9] 138—140°C). Yield, 55%.

3-Ferrocenyl-1-(*p*-tolyl)-2-propen-1-one (2b). The crude product (92.4% yield) was recrystallized from ethanol to give violet needles; mp 138.5—139.5°C. λ_{max} (95% ethanol) 277.5, 326, 398(sh) and 514 mμ.

Found: C, 72.55; H, 5.59%. Calcd for $C_{20}H_{18}OFe$: C, 72.82; H, 5.46%.

3-Ferrocenyl-1-(*p*-anisyl)-2-propen-1-one (2c). The crude product (80.7% yield) was recrystallized from ethanol to afford purple needles; mp 154.5—155.5°C. λ_{max} (95% ethanol) 279, 327, 390 and 512 mμ.

Found: C, 69.40; H, 5.21%. Calcd for $C_{20}H_{15}O_2Fe$: C, 69.39; H, 5.20%.

3-Ferrocenyl-1-(*p*-chlorophenyl)-2-propen-1-one(2d). The recrystallization of crude **2d** (88.2% yield) from ethanol gave reddish-orange needles; mp 167—168°C. λ_{max} (95% ethanol) 273, 330, 396 and 520 mμ.

Found: C, 65.08; H, 4.40%. Calcd for $C_{19}H_{15}OClFe$: C, 65.08; H, 4.28%.

3-Ferrocenyl-1-(*p*-nitrophenyl)-2-propen-1-one (2e). On the recrystallization of crude **2e** (8.47% yield) from chloroform - ether (2 : 1), violet needles were obtained; mp 228—230°C. λ_{max} (95% ethanol) 270, 337, 410(sh) and 546 mμ.

Found: C, 62.80; H, 4.28; N, 3.93%. Calcd for $C_{19}H_{15}O_3NFe$: C, 63.18; H, 4.16; N, 3.88%.