On Ferrocene Derivatives. XXI.
Elucidation of Structure of Various Acetylated Derivatives of Ferrocene by Infrared Spectroscopy

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The investigation of 77 ferrocene derivatives by infrared spectroscopy showed that the rule of Rosenblum is valid for all monosubstituted and 1,1'-disubstituted derivatives. When acetyl group is one of the substituents in an 1,1'-disubstituted compound, a moderately intense absorption band appears in the $1113-1122$ cm^{-1} region. The presence of this band could be used as a proof of the 1,1'-disubstitution in ferrocene, even when an additional ferrocene radical possessing one ring unsubstituted is a part of the molecule. In such cases the rule of Rosenblum does not enable to distinguish 1,1'-, 1,2- or 1,3-dispositions of substituents of a monoacetyl derivative.

The differentiation between homoannular and heteroannular substitution in ferrocene by infrared spectroscopy was the subject of numerous studies [1—15]. In order to establish the substitutions in ferrocene derivatives, *Rosenblum* [1] used the absorption bands resulting from the breathing vibration of cyclopentadiene rings near 1100 cm^{-1} and the C—H deformation mode near 1000 cm^{-1}. When one of the cyclopentadiene rings is unsubstituted, both 1100 and 1000 cm^{-1} are observed in the infrared spectrum. As for those derivatives, in which both cyclopentadiene rings possess substituents, the above mentioned bands are not present. This empirical generalization, called also the 1100 and 1000 cm^{-1} rule of Rosenblum, was verified on series of substituted ferrocenes by several authors [2—9]. In some papers [10, 11] exceptions of the rule were reported. These were predominantly due to the absorption of substituents. An absorption band near 1000 cm^{-1} has been also observed in the spectra of heteroannularly disubstituted ferrocene derivatives [12—15]. The absence of the 1100 cm^{-1} band in the spectra of such derivatives could be reliably used for the identification of 1,1'-disubstitution. Thus the previous deviation from the rule does not restrict its validity.

Investigating the substituents dispositions in acetylated alkyl derivatives of ferrocene, *Rosenblum* and *Woodward* [4] found that the derivatives having the acetyl group on an unsubstituted cyclopentadiene ring exhibited absorption bands near 1115 cm^{-1}. These bands were not observed in the spectra of those acetylated derivatives, which possessed another acetyl group on the same cyclopentadiene ring at 2- or 3-position. The authors did not give the assignment for these absorption bands. The spectra of acetyl and 1,1'-diacetylferrocene were interpreted in detail by *Pavlík* and *Handlíř* [16] in the study on donor-acceptor complexes of these two basic

ferrocene derivatives. The 1115 cm^{-1} absorption band, occuring in the spectra of both derivatives, was attributed to the symmetric vibration of the two carbons of acetyl group and the cyclopentadiene ring carbon.

Experimental

The compounds *1—54* (Table 1) were synthesized as described previously [17, 18].

1,1'-Bis(3-nitrophenyl)ferrocene *(73)* and 1,1'-bis(3-acetylphenyl)ferrocene *(76)* were prepared by arylation of ferrocene with corresponding diazonium salts. In the case of the former derivative crystallized from benzene:

for C$_{22}$H$_{16}$FeN$_2$O$_4$ (428.2) calculated: 13.04% Fe, 6.54% N; found: 13.01% Fe, 6.47% N; m.p. 222—224°C;

for the later derivative crystallized from acetone—petroleum ether: for C$_{26}$H$_{22}$FeO$_2$ (422.3) calculated: 13.22% Fe; found: 13.29% Fe; m.p. 145—147°C.

The compounds *67, 70—72* were synthesized according to [19, 20]; their melting points were in a good agreement with those reported in the above quoted references.

Infrared spectra were measured with a double-beam UR-20 spectrophotometer (Zeiss, Jena) in the 650—2000 cm^{-1} region. The wavelength scale of the monochromator was calibrated according to the standard spectra of polystyrene and the mixture of indene, cyclohexanone and camphor [21]. The spectra of solids were recorded from paraffin oil mulls of 0.02 mm thickness. The spectra of liquids were recorded from thin-layers of about 0.01 mm thickness. The frequencies in the range of 1000—1150 cm^{-1} were evaluated with an accuracy of ± 1 cm^{-1}. Those corresponding to significant absorption bands are listed in Table 1.

Results and Discussion

The most important infrared absorption bands to differentiate between homoannular and heteroannular substitution in ferrocene (Formula 1) are those near 1000 and 1100 cm^{-1}.
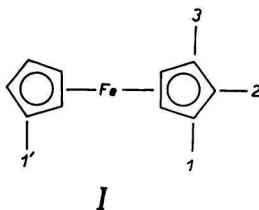

Formula 1

We drew attention to these two absorption bands of 77 ferrocene derivatives, major part of them being acetyl derivatives (Table 1). The table includes absorption bands of some basic ferrocene derivatives, which the corresponding acetyl derivatives were prepared from. Characteristic frequencies of several other ferrocene derivatives are listed as well, as a suplement to the conclusions of this work.

All 44 ferrocene derivatives having at least one unsubstituted cyclopentadiene ring exhibit two absorption bands in the range of 1000—1010 cm^{-1} and 1103——1111 cm^{-1}. All these compounds behave thus according to the rule of Rosenblum.

27 of 33 ferrocene derivatives with substituents displaced on all cyclopentadiene rings failed to absorb in the $1103-1111$ cm^{-1} region. The first exceptions of this group are two derivatives which contain in molecule the nitro group attached to benzene ring (substances 72 and 73). These compounds showed a week absorption band in the range of $1105-1110$ cm^{-1}. Since the corresponding derivatives without the nitro group lack the above mentioned band, the absorption of the samples 72 and 73 near 1100 cm^{-1} apparently results from the presence of nitro group and not from the vibration of cyclopentadiene rings. Most of the substituted nitro benzenes also exhibit absorption bands near 1100 cm^{-1} [22]. The third exception of the 33 heteroannularly substituted ferrocenes was found to be 1,1'-dipropionylferrocene (63) showing an absorption band at 1103 cm^{-1}. A similar behaviour of 1,1'-diiso-propylferrocene has been reported elsewhere [4].

32 heteroannularly substituted ferrocenes exhibit, however, an absorption band in the $1001-1027$ cm^{-1} region. This band has been usually found to be shifted to higher frequencies regarding the bands near 1000 cm^{-1} of analogous homoannularly substituted derivatives. Such deviations from the rule of Rosenblum were also observed in the spectra of various 1,1'-disubstituted ferrocenes [12—15]. It can be stated therefore that all heteroannularly substituted derivatives under our investigation behave according to the rule of Rosenblum; they do not absorb in the $1103-1111$ cm^{-1} region.

Besides the absorption bands used according to the rule for the differentiation of homoannular and heteroannular substitution we have observed a further weak absorption band in the range of $1113-1122$ cm^{-1} in the spectra of all 21 hetero-annularly substituted ferrocene derivatives containing acetyl group at 1- or 1'-position. This band also occurs in the spectrum of acetylferrocene (compound 55), but is not exhibited by 1-substituted 2-acetyl derivatives (compounds 14, 22, 25, 43, 52 and 53). As reported by Rosenblum and Woodward [4], neither 2-acetyl- nor 3-acetyl--1,1'-dialkyl derivatives of ferrocene exhibited this absorption band. Absorption bands in this region are also absent in the spectra of 2-acetylthiophene, 2-acetylfurane and substituted 2-acetylthiophenes [23]. In this regard, as exceptions were found to be some ferrocene derivatives in which the acetyl group is linked to benzene ring, as (4-acetylphenyl)ferrocene and 1,1'-bis(3-acetylphenyl)ferrocene (compounds 75 and 76). It may be concluded from the above-said, that the absorption band we have observed in the $1113-1122$ cm^{-1} region, is due to the vibration of the acetyl group bound to the ferrocene skeleton at 1- or 1'-position. This is further confirmed by the fact, that substances as methylferrocene, 1,1'-diethylferrocene, ferrocene-carboxylic acids, ferrocenecarboxaldehyde, 1,1'-dipropionylferrocene, benzoyl derivatives of ferrocene and [5]ferrocenophane-1,5-diones, fail to exhibit absorption in this region. The 1115 cm^{-1} absorption band of acetylferrocene and 1,1'-diacetyl-ferrocene was ascribed to the symmetric vibration of the acetyl group carbons and the cyclopentadiene ring carbon [16], as outlined in Schema 1:

$$C_{ring}$$
$$\downarrow \|$$
$$C_{acetyl}$$
$$\nearrow$$
$$H_3C \qquad \nu_s \sim 1115 \text{ cm}^{-1}$$
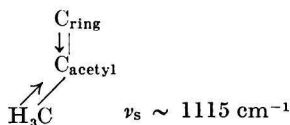
Schema 1

Table 1

No.	Compound	ω_{18}	ω_{10}	$\nu(\mathrm{C-CH_3})$
		1000—1010 cm⁻¹	1103—1111 cm⁻¹	1113—1122 cm⁻¹
1	1-ferrocenyl-3-phenyl-2-propene-1-one	1004	1108	—
2	1-(1'-acetylferrocenyl)-3-phenyl-2-propene-1-one	1010	—	1116
3	1-ferrocenyl-3-(2-thienyl)-2-propene-1-one	1004	1106	—
4	1-ferrocenyl-3-(5-acetyl-2-thienyl)-2-propene-1-one	1003	1106	—
5	1-(1'-acetylferrocenyl)-3-(2-thienyl)-2-propene-1-one	1008	—	1113
6	1-ferrocenyl-3-(2-furyl)-2-propene-1-one	1007	1109	—
7	1-ferrocenyl-3-(5-acetyl-2-furyl)-2-propene-1-one	1007	1108	—
8	1-(1'-acetylferrocenyl)-3-(2-furyl)-2-propene-1-one	1008	—	1117
9	1,3-diferrocenyl-2-propene-1-one	1008	1107	—
10	1-ferrocenyl-3-(1'-acetylferrocenyl)-2-propene-1-one	1006	1106	1117
11	1-(1'-acetylferrocenyl)-3-ferrocenyl-2-propene-1-one	1008	1107	1117
12	1,3-bis(1'-acetylferrocenyl)-2-propene-1-one	1013	—	1117
13	3-ferrocenyl-1-phenyl-2-propene-1-one	1010	1109	—
14	3-(2-acetylferrocenyl)-1-phenyl-2-propene-1-one	1006	1106	—
15	3-(1'-acetylferrocenyl)-1-phenyl-2-propene-1-one	1018	—	1117
16	3-ferrocenyl-1-(2-thienyl)-2-propene-1-one	1009	1109	—
17	3-ferrocenyl-1-(5-acetyl-2-thienyl)-2-propene-1-one	1005	1109	—
18	3-(1'-acetylferrocenyl)-1-(2-thienyl)-2-propene-1-one	1023	—	1118
19	3-(1',2-diacetylferrocenyl)-1-(2-thienyl)-2-propene-1-one	1022	—	1116
20	3-ferrocenyl-1-(2-furyl)-2-propene-1-one	1010 sh	1110	—
21	3-ferrocenyl-1-(5-acetyl-2-furyl)-2-propene-1-one	1002	1107	—
22	3-(2-acetylferrocenyl)-1-(2-furyl)-2-propene-1-one	1007	1105	—
23	3-(1'-acetylferrocenyl)-1-(2-furyl)-2-propene-1-one	1015	—	1118
24	1-ferrocenyl-2-phenylethene	1003	1106	—
25	1-(2-acetylferrocenyl)-2-phenylethene	1008	1106	—
26	1-ferrocenyl-2-(2-thienyl)ethene	1004	1103	—
27	1-ferrocenyl-2-(5-acetyl-2-thienyl)ethene	1003	1109	—
28	1-(1'-acetylferrocenyl)-2-(5-acetyl-2-thienyl)ethene	1023 sh	—	1117
29	1-ferrocenyl-2-(2-furyl)ethene	1005	1106	—
30	1-ferrocenyl-2-(5-acetyl-2-furyl)ethene	1005	1105	—

Table 1 (Continued)

No.	Compound	ω_{18} 1000—1010 cm⁻¹	ω_{10} 1103—1111 cm⁻¹	ν(C—CH₃) 1113—1122 cm⁻¹
31	1,2-diferrocenylethene	1005	1105	—
32	1-(1'-acetylferrocenyl)-2-ferrocenyl-ethene	1004	1105	1114
33	benzoylferrocene	1007	1109	—
34	1-acetyl-1'-benzoylferrocene	1007 sh	—	1117
35	(2-thienoyl)ferrocene	1008	1110	—
36	1-acetyl-1'-(2-thienoyl)ferrocene	1025	—	1118
37	(2-furoyl)ferrocene	1006	1110	—
38	1-acetyl-1'-(2-furoyl)ferrocene	1024	—	1117
39	ferrocenoylferrocene	1003	1009	—
40	1-acetyl-1'-ferrocenoylferrocene	1009	1108	1117
41	(1'-acetylferrocenoyl)(1'-acetylferro-cene)	1020	—	1116
42	benzylferrocene	1004	1108	—
43	2-acetyl-1-benzylferrocene	1006	1108	—
44	1-acetyl-1'-benzylferrocene	1008	—	1119
45	(2-thienylmethyl)ferrocene	1005	1107	—
46	(5-acetyl-2-thienylmethyl)ferrocene	1004	1107	—
47	1-acetyl-1'-(5-acetyl-2-thienyl)ferro-cene	—	—	1115
48	(2-furylmethyl)ferrocene	1008	1110	—
49	(5-acetyl-2-furylmethyl)ferrocene	1004	1107	—
50	1-acetyl-1'-(5-acetyl-2-furylmethyl)-ferrocene	1022	—	1122
51	ferrocenylmethylferrocene	1002	1104	—
52	(2-acetylferrocenylmethyl)ferrocene	1004	1105	—
53	2-acetyl-1'-(2-acetylferrocenyl-methyl)ferrocene	1003	1104	—
54	1-acetyl-1'-(1'-acetylferrocenyl-methyl)ferrocene	1025	—	1116
55	acetylferrocene	1010	1105	1119
56	1,1'-diacetylferrocene	1025	—	1120
57	ferrocenecarboxylic acid	1010	1111	—
58	1,1'-ferrocenedicarboxylic acid	1025 sh	—	—
59	ferrocenecarboxaldehyde	1005	1108	—
60	hydroxymethylferrocene	1000	1105	—
61	methylferrocene	1002	1107	—
62	1,1'-diethylferrocene	1022	—	—
63	1,1'-dipropionylferrocene	1027	1103	—
64	1,1'-dibenzoylferrocene	1001 sh	—	—
65	[5]ferrocenophane	1020 sh	—	—
66	3-phenyl[5]ferrocenophane-1,5-dione	1005 sh	—	—
67	3-(2-thienyl)[5]ferrocenophane-1,5-dione	—	—	1123
68	3-(2-furyl)[5]ferrocenophane-1,5-dione	1015	—	—
69	1-(1'-phenylacetylferrocenyl)-3-phenyl-2-propene-1-one	1011 sh	—	—
70	1-(1'-benzoylferrocenyl)-3-phenyl-2-propene-1-one	1015	—	—
71	1-(1'-benzoylferrocenyl)-3-ferro-cenyl-2-propene-1-one	1005 (1011)	1111	—

Table 1 (Continued)

| No. | Compound | ω_{18} | ω_{10} | $\nu(\text{C—CH}_3)$ |
		1000—1010 cm^{-1}	1103—1111 cm^{-1}	1113—1122 cm^{-1}
72	1-(1′-benzylferrocenyl)-3-(3-nitro-phenyl)-2-propene-1-one	1019 sh	1105 sh	—
73	1,1′-bis(3-nitrophenyl)ferrocene	1022	1110	—
74	(3-acetylphenyl)ferrocene	1004	1108	—
75	(4-acetylphenyl)ferrocene	1007	1108	1116 sh
76	1,1′-bis(3-acetylphenyl)ferrocene	1025	—	1117
77	1,1′-bis(4-acetylphenyl)ferrocene	1017	—	1120

The symbols ω_{18} and ω_{10} denote the vibrations of ferrocene rings according to *Lippincott* and *Nelson* [25].

The designation $\nu(\text{C—CH}_3)$ is used for the vibration shown in Schema 1.

All absorption bands listed in the table are weak or moderately intense and are given in cm^{-1}.

sh = a shoulder on the adjacent absorption band.

The 1113—1122 cm^{-1} absorption band thus affords the opportunity to confirm the heteroannular substitutions of ferrocene derivatives under the condition that the molecule does not contain an acetylated benzene ring.

We exploited this empirical finding for the elucidation of the structures of compounds obtained by acetylation of derivatives formed from two ferrocene skeletons chained together. The rule of Rosenblum does not enable to distinguish between homoannular and heteroannular substitution in one of the ferrocenes of the mono-acetylated derivative of this type, since all these derivatives give absorption bands in the range of 1000—1010 cm^{-1} and 1103—1111 cm^{-1}. The presence of the 1113—1122 cm^{-1} band, however, could be used as a proof that compounds *10, 11, 32* and *40* possess one heteroannularly acetylated ferrocene skeleton. On the other hand, substances *52* and *53* lacking the absorption band at 1113—1122 cm^{-1} do not contain therefore a heteroannularly acetylated ferrocene skeleton.

Based upon the presence of the 1116—1117 cm^{-1} band and using the rule of Rosenblum the derivatives *12, 41* and *54* were unambiguously specified as having both ferrocene skeletons heteroannularly acetylated. The structures of compounds *2, 5, 8* and *10* were also confirmed preparatively by intramolecular Michael addition [17]. The structures of the derivatives containing benzene, thiophene and furane were established on the basis of their absorption in the 650—900 cm^{-1} region as well.

Finally, we consider to be of interest to remark we tried to verify the 927 and 894 cm^{-1} rule for 1,2-substitution of ferrocene derivatives [5, 6, 24]. This was found not to be generally valid for compounds under our investigation. Almost all derivatives, namely monosubstituted and 1,1′-disubstituted ferrocenes, showed an absorption at 927 and 894 cm^{-1}.

References

1. Rosenblum M., *Thesis*. Harvard University, 1953.
2. Pauson P. L., *J. Amer. Chem. Soc.* **76**, 2184 (1954).
3. Reinhart K. L., Curby R. J., Sokol E., *J. Amer. Chem. Soc.* **79**, 3420 (1957).

4. Rosenblum M., Woodward R. B., *J. Amer. Chem. Soc. 80*, 5443 (1958).
5. Rosenblum M., *J. Amer. Chem. Soc. 81*, 4530 (1959).
6. Rosenblum M., Howells W. G., *J. Amer. Chem. Soc. 84*, 1167 (1962).
7. Nesmejanov A. N., Kazicina L. A., Lokšin B. V., Krickaja I. I., *Dokl. Akad. Nauk SSSR 117*, 433 (1957).
8. Hadlington M., Rockett B. W., Nelhans A., *J. Chem. Soc. C1967*, 1436.
9. Dvorjanceva G. G., Šejnker J. N., Jureva L. P., Nesmejanov A. N., *Dokl. Akad. Nauk SSSR 156*, 873 (1964).
10. Mayley E. A., Dickey C. R., Goodale G. M., Matthews V. E., *J. Org. Chem. 27*, 616 (1962).
11. Goldberg S. I., Mayo D. W., Vogel M., Rosenberg H., Rausch M., *J. Org. Chem. 24*, 824 (1959).
12. Neuse E. W., Trifan D. S., *J. Amer. Chem. Soc. 84*, 1850 (1962).
13. Nesmejanov A. N., Vilčevskaja V. D., Makarova A. I., *Dokl. Akad. Nauk SSSR 169*, 351 (1966).
14. Nesmejanov A. N., Drozd V. N., Sazonova V. A., *Izv. Akad. Nauk SSSR, Ser. Chim. 1965*, 1205.
15. Hall D. W., Richards I. H., *J. Org. Chem. 28*, 1549 (1963).
16. Pavlík I., Handlíř K., *Collect. Czech. Chem. Commun. 31*, 1958 (1966).
17. Toma Š., *Collect. Czech. Chem. Commun. 34*, 2235 (1969).
18. Toma Š., Kalužayová E., *Chem. Zvesti 23*, 540 (1969).
19. Toma Š., *Chem. Zvesti 19*, 703 (1965).
20. Rosenblum M., *Chemistry of the Iron Group Metallocenes*, Part I, p. 91, 153. J. Wiley, New York, 1965.
21. Jones R. N., Fauer P. K., Zacharias W., *Rev. Univers. Mines, 15*, 417 (1959).
22. Colthup N. B., Daly L. H., Wiberley S. E., *Introduction to Infrared and Raman Spectroscopy*, p. 391. Academic Press, New York—London, 1964.
23. Boľšakov G. F., Glebovskaja E. A., Kaplan Z. G., *Infrakrasnyje spektry i rentgenogramy geteroorganičeskich sojedinenij*, p. 55—56. Izdateľstvo Chimija, Leningrad, 1967.
24. Nagai Y., *Bull. Chem. Soc. Jap. 37*, 53 (1964).
25. Lippincott E. R., Nelson R. D., *Spectrochim. Acta 10*, 307 (1958).

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