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Structural formulas I and II

Figure 1: Structural formulas I and II

Abstract

Full Text

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DETERMINATION OF THE POSITIONS OF SUBSTITUENTS IN FERROCENE COMPOUNDS FROM INFRARED ABSORPTION SPECTRA

To the present time several reports have been published on the infrared spectra of ferrocene and its derivatives ([1–8]). Apparently, we possess the largest series of infrared spectra of substances of this series, described by one of us with co-workers ([9–16]). Comparison of these data enables us to arrive at conclusions, which constitute the subject of the present communication, concerning the correspondence of the infrared spectra of ferrocene derivatives to certain features of their structure. These conclusions have served us as an important means for establishing the structure of ferrocene homologs obtained by direct alkylation of ferrocene by means of the Friedel-Crafts reaction. In addition, they made it possible to refine the structure of the products, obtained by one of us with Kritskaya ([16]), of the condensation of formaldehyde and other aldehydes with ferrocene, containing two ferrocene rings linked by two methylene (respectively, benzylidene) groups.

By the present time, one of us and E. G. Perevalova with co-workers ([17]) have developed two chemical methods for establishing the position of substituents in ferrocene derivatives, each of which has its own limitations. The first (catalytic hydrogenation under severe conditions) leads to the corresponding cyclopentane derivatives. The second (bromination) leads to the formation of pentabromocyclopentane in the case of those ferrocene derivatives that have one unsubstituted cyclopentadienyl ring. This latter method is identical, in the range of its application, with the method substantiated here for establishing the same structural feature on the basis of infrared spectra, and in the present work the correspondence of the two methods is established. Thus, the condensation products of ferrocene with formaldehyde (and other aldehydes), on the basis of application of both methods, prove to have unsubstituted cyclopentadienyl rings and, consequently, the structure expressed by formula I, and not the isomeric II.

I

II

The infrared spectra of ferrocene compounds, as Lippincott and Nelson ([3]) have shown, are distinguished by simplicity owing to the high symmet-

of the molecule, and in addition to the C–H stretching vibrations in the region 3000-3100 cm^{-1}, there are only four sufficiently intense bands: the frequencies at 811 and 1001 cm^{-1} in ferrocene arise as a result of C–H–

Table 1

No.	Compound	ν, cm^{-1}	Source
1	$C_5H_5FeC_5H_5$	1004; 1110	–
2	$C_5H_5FeC_5H_4CH_3$	1004; 1109	([9])
3	$C_5H_5FeC_5H_4CH(CH_3)_2$	1003; 1107	([9])
4	$C_5H_5FeC_5H_4C(CH_3)_3$	1000; 1106	([9])
5	$C_5H_5FeC_5H_4C_6H_4CH_3$	1001; 1107	([10])
6	$C_5H_5FeC_5H_4COCH_3$	1005; 1105	([11])
7	$C_5H_5FeC_5H_4COOH$	1006; 1108	([11])
8	$C_5H_5FeC_5H_4COOCH_3$	1005; 1108	([11])
9	$C_5H_5FeC_5H_4(CH_2)_3COOH$	1002; 1104	([20])
10	$C_5H_5FeC_5H_4CO(CH_2)_2COOH$	1006; 1106	([20])
11	$C_5H_5FeC_5H_4CO(CH_2)_2COOCH_3$	1000; 1105	([20])
12	$C_5H_5FeC_5H_4NHCOCH_3$	1001; 1104	([12])
13	$C_5H_5FeC_5H_4COC_6H_4COOH$	1005; 1105	([13])
14	$C_5H_5FeC_5H_4COC_6H_4OCH_3$	1000; 1104	([13])
15	$C_5H_5FeC_5H_4C_6H_4NO_2$	1000; 1106	([10])
16	$C_5H_5FeC_5H_4C(CH_3)=CH_2$	1002; 1104	–
17	$CH_3C_5H_4FeC_5H_4CH_3$	–	([14])
18	$C_2H_5C_5H_4FeC_5H_4C_2H_5$	–	([15])
19	$CH_2OHC_5H_4FeC_5H_4CH_2OH$	–	([14])
20	$CH_3C_6H_4C_5H_4FeC_5H_4C_6H_4CH_3$	–	–
21	$CH_3COOC_5H_4FeC_5H_4COOCH_3$	–	([11])
22	$CH_3COC_5H_4FeC_5H_4COOCH_3$	–	([18])
23	$C_3H_7COC_5H_4FeC_5H_4COOCH_3$	–	([18])

No.	Compound	ν, cm^{-1}	Source
24	[[structural formula diagram: ferrocene derivative with a fused cyclic anhydride-like fragment labeled CO, CO, CH_2, CH_2 on one cyclopentadienyl ring]]	999; 1104	([13])
25	[[structural formula diagram: ferrocene derivative with a fused cyclic diketone/anhydride-like fragment labeled CO, CO, fused to a benzene ring on one cyclopentadienyl ring]]	1003; 1107	([20])
26	[[structural formula diagram: diferrocenyl compound with two ferrocene units linked through a $-CH_2-CH_2-$ bridge between substituted cyclopentadienyl rings]]	1005; 1104	([16])

No.	Compound	ν, cm^{-1}	Source
27	[[structural formula diagram: diferrocenyl compound with two ferrocene units linked through two CH groups; each CH bears C_6H_5]]	1004; 1106	([16])
28	[[structural formula diagram: diferrocenyl compound with two ferrocene units linked through CH and $CH{-}OH$; substituents $C_6H_4N(CH_3)_2$ and $C_6H_4N(CH_3)_2$ attached to the CH centers]]	999; 1105	–
29	$C_5H_5FeC_5H_3(CH_3)_2$	1004; 1107	([9])
30	$C_5H_5FeC_5H_3(C_2H_5)_2$	998; 1107	([9])
31	$C_5H_5FeC_5H_3(C_2H_5)_2$	998; 1107	([9])
32	$C_5H_5FeC_5H_3(CH(CH_3)_2)_2$	1002; 1107	
	$C_5H_5FeC_5H_3(C(CH_3)_3)_2$	1000; 1107	

deformation vibrations; the frequency 1108 cm^{-1} is an antisymmetric ring vibration, and the frequency 1411 cm^{-1} represents an antisymmetric stretching vibration of the C–C bond. The most intense bands among those indicated correspond to the frequencies at 1002 and 1108 cm^{-1}. These were therefore chosen by us as the criteria for determining the position of substituents in ferrocene compounds.

The spectra were recorded on a single-beam IR spectrometer IKS-II, with recording on paper tape by means of an electronic potentiometer EPP-09. Solid samples were recorded as a paste in Vaseline oil, and liquids were recorded neat,

with a layer thickness of 0.05 mm.

We recorded the spectra of ferrocene and of 15 monosubstituted ferrocenes with substituents of very diverse structure (Table 1, Nos. 1-16).

We also recorded the spectra of 7 disubstituted ferrocene compounds in which the substituents were known to be located in different rings, as had previously been shown chemically (Table 1, Nos. 17-23). In the spectra of these compounds, the frequencies 1002 and 1107 cm^{-1} were not observed.

In the spectra of compounds 24-28 (Table 1), intense bands with frequencies 1002 and 1107 cm^{-1} were found, which indicated the presence of a free cyclopentadienyl ring.

For compounds 26, 27, and 28 the presence of a free cyclopentadienyl ring was also confirmed chemically by the bromination reaction.

On treatment of all three indicated substances with an excess of bromine in carbon tetrachloride at the boiling temperature of the latter, we isolated pentabromocyclopentane, m.p. 83-101° (mixture of stereoisomers) ([17]). For the condensation product of ferrocene with formaldehyde, the yield of pentabromocyclopentane was 43% of theory, calculated for two unsubstituted cyclopentadienyl rings in the molecule. The condensation products with aromatic aldehydes (27, 28) decomposed with greater difficulty under the same conditions, and only a small yield of pentabromocyclopentane was obtained. It should also be noted that for compound 28 (m.p. 257°), along with the other characteristic frequencies, the frequency 1350 cm^{-1}, characteristic of deformation vibrations of the hydroxyl group, was also found; this confirms the open-chain structure proposed for it.

Disubstituted ferrocenes (29-33) (Table 1) contain in their spectra the frequencies 1002 and 1107 cm^{-1}, which may be regarded as proof of the presence of a free cyclopentadienyl ring.

The infrared spectra available in the literature for 1,2-ferrocenedicarboxylic acid, its ester, and its anhydride also have the frequencies 1000-1002 and 1102-1116 cm^{-1} ([7]).

Comparison of two isomeric ethylferrocenes substituted in one ring (n_D^{20} 1.5820 and n_D^{20} 1.5847) showed that their spectra are analogous, with the exception of the frequency 1277 cm^{-1}, which appears in only one of these compounds.

Table 2

Nos. in Table 1	ν of carbonyl group, cm^{-1}	Nos. in Table 1	ν of carbonyl group, cm^{-1}
6	1660	22	1657
10	1660	23	1661
11	1670	24	1678
13	1650	25	1657
14	1650		

Nos. in Table 1	ν of carbonyl group, cm^{-1}	Nos. in Table 1	ν of carbonyl group, cm^{-1}

Work on the determination of isomers disubstituted in one ring is continuing.

For ferrocene compounds containing a carbonyl group conjugated with the ferrocene ring, the values of the frequencies of the C = O group were examined (Table 2).

It is seen from Table 2 that the frequency of the ketone C=O lies in the region 1650-1678 cm^{-1}, which indicates a considerable shift of the C = O frequency relative to the corresponding aliphatic carbonyl compounds and may be explained by conjugation of the carbonyl with the cyclopentadienyl ring. This is-

decrease is analogous to the shift of the carbonyl frequency from 1710 cm^{-1} in acetone to 1685 cm^{-1} in acetophenone (19), due to conjugation with the aromatic ring.

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Note: Figure translations are in progress. See original paper for figures.