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(CYCLOHEXA-1,3-DIENE- AND (4-FERROCENYLBUTA-1,3-DIENE-IRON TRICARBONYL) CARBOXYLIC ACID NITRILES

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Summary

The relative reactivity of the —C≡N group in different positions of cyclohexadiene ligand was investigated by Pinner's reaction. The nitrile group was shown to be inert in Pinner, Stefen and Grignard reactions for 1,2,3,4-h^4-2-methyl-4-ferrocenylbutadienecarbonitrileiron tricarbonyl. The behaviour of the —C≡N group in these complexes may largely be explained by steric factors due to the presence of the iron tricarbonyl fragment. The reactivities of the —C≡N group in α,β-disubstituted ethylenes and their vinyl analogs ferrocenylbutadiene are essentially different.

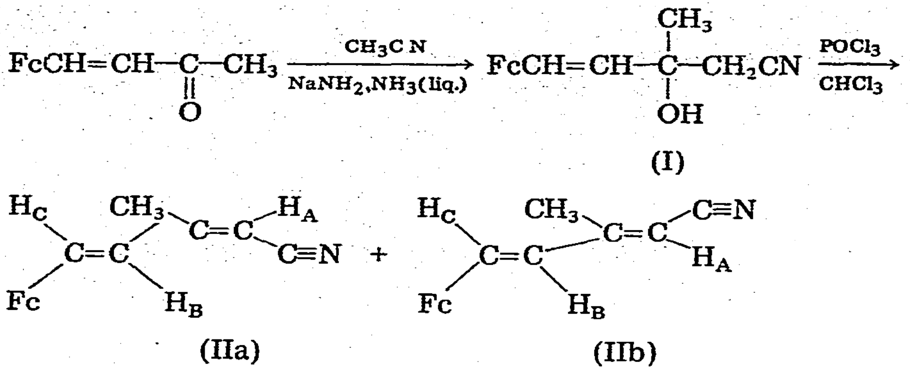
Results and discussion

(4-Ferrocenylbuta-1,3-dieneiron tricarbonyl) carboxylic acid nitriles

The formation of 2-*cis*,4-*trans*- (IIa) and 2-*trans*,4-*trans*- (IIb) isomers of 2-methyl-4-ferrocenylbuta-1,3-diene carboxylic acid nitrile and the preparation of the respective complexes IIIa and IIIb of 1,2,3,4-h^4-2-methyl-4-ferrocenylbutadienecarbonitrileiron tricarbonyl have been described in our earlier paper [1] on the study of the reaction of 2-hydroxy-2-methyl-4-ferrocenylbut-3-enecarbonitrile (I) with $Fe_3(CO)_{12}$.

In the present work the synthesis of IIa and IIb was carried out according to eq. 1.

Condensation of ferrocenalacetone with CH_3CN in the presence of $NaNH_2$ in liquid NH_3 was carried out under conditions similar to those described for formylferrocene [2]. Dehydration of I in the presence of $POCl_3$ in $CHCl_3$ at an elevated temperature afforded a mixture of two products (1/3). Elemental analysis for each of the products is in good agreement with the empirical formula $C_{16}H_{15}FeN$. Unlike the *cis*- and *trans*-isomers of β-ferrocenylacrylonitrile the dehydration products isolated in the present work exhibit practically identical IR spectra.



(1)

$(Fc = C_5H_5FeC_5H_4—)$

To elucidate the configuration of the isomers IIa and IIb obtained we studied their PMR and UV spectra. The PMR spectra of these isomers show a doublet from the methyl group, a sharp singlet from five equivalent C_5H_5 protons and two triplets from C_5H_4, as well as two downfield doublets from vinyl protons.

The spin—spin coupling constants of protons H_B and H_C for compounds IIa and IIb are equivalent (15.6 Hz), i.e. they are *trans*-located with respect to the double bond. Owing to long-range spin—spin coupling with the methyl protons the signal of the H_A olefin proton is split into a quartet with spin—spin coupling constant $J(H_A—CH_3)$ 1.4 Hz for IIa and $J(H_A—CH_3)$ 0.8 Hz for IIb. Thus the upfield methyl signal for the two isomers is a doublet with δ 2.06 ppm for IIa and δ 2.25 ppm for IIb. Under the second radiofrequency field of the H_A proton the methyl group doublet transforms into a singlet. This confirms that the H_A proton is coupling with the methyl protons. Some variation of the chemical shifts may be explained by different methyl group environments: in IIa the methyl protons are not subject to the anisotropic effect of the $—C{\equiv}N$ neighbour, and in IIb the $C{\equiv}N$ group is *cis*-located with respect to the methyl protons and may cause deshielding, thus their signal would be downfield. The H_A proton shielding may be due to a significant diamagnetic anisotropy of the $—C{\equiv}N$ triple bond [3]. Our results are confirmed by the literature data on the configuration of the geometric isomers of 3-methyl-5-phenylpenta-2,4-diene acid methyl ester elucidated by means of PMR study [4].

Thus the difference of the $H_A—CH_3$ spin—spin coupling constants (Δ 0.6 Hz) and the methyl group chemical shifts (Δ 0.19 ppm) may serve as proof that compounds IIa and IIb are geometric isomers. Signal positions and splitting patterns

TABLE 1

CHEMICAL SHIFTS (δ PPM) AND SPIN—SPIN COUPLING CONSTANTS (Hz) OF IIa AND IIb PROTONS

Compound	H_A	H_B	H_C	CH_3	C_5H_5	C_5H_4	$J(H_C—H_B)$	$J(H_A—CH_3)$
IIa	5.02	6.66	6.91	2.06	4.06	4.27	15.6	1.4
IIb	5.14	6.39	6.66	2.25	4.06	4.33	15.6	0.8

TABLE 2

MAXIMA (λ (nm) AND INTENSITIES (ϵ lmol^{-1} cm^{-1}) IN THE ABSORPTION SPECTRA OF *cis,trans*- AND *trans,trans*-2-METHYL-4-FERROCENYLBUTA-1,3-DIENECARBONITRILE ISOMERS [a]

Band	*cis, trans*- IIa		*trans, trans*- IIb	
	λ	$\epsilon \times 10^3$	λ	$\epsilon \times 10^3$
1	213	21.3	212	22.4
2	273	10.2	271	14
3	323	23.1	321	30.7
4	486	2.2	460	2.8

[a] In the region of 380—390 nm the spectra of IIa and IIb display shoulders with ϵ ca. 2.5×10^3.

allow it to be assumed that compound IIa is the 2-*cis*, 4-*trans*-isomer of 2-methyl-4-ferrocenylbuta-1,3-dienecarbonitrile, while compound IIb is 2-*trans*, 4-*trans*-2-methyl-4-ferrocenylbuta-1,3-dienecarbonyl.

The UV spectra provided additional information on the structure of these isomers. It is known that in *trans*-isomers in the most simple cases the absorption corresponding to $\pi \rightarrow \pi^*$ transitions is usually observed at a longer wavelength and with higher extinction coefficients than *cis*-isomers. The compounds investigated contain several different chromophore groups and one would expect more complicated dependences in their spectra. Experiment shows (Table 2) that one of the isomers (e.g. IIb), which we discussed as a *trans*, *trans* species, has greater absorption intensity at all wavelengths which is in agreement with the above assignment to the more "elongated" *trans,trans*-isomer. It is specific of the spectra that the principal band positions show practically no alteration on going from one isomer to the other. Only a transition band position alters, undergoing a hypsochromic shift of 26 nm on going from IIa to IIb. Thus unlike IR spectra the PMR and UV spectra of the substituted butadienes provide valuable information on geometry of the isomers investigated.

We studied the reactivities of the isomers obtained. We noticed in particular that they do not change under the conditions of Stefen's reaction unlike the *cis*- and *trans*-isomers of β-ferrocenylacrylonitrile * where the *cis*-isomer transformed quantitatively into the *trans* isomer [5].

Hydration with an alkaline alcohol solution and hydrogen peroxide converts each isomer into the amide (IV) and an equilibrium mixture of IIa and IIb (eq. 2).

$$\left.\begin{matrix}\text{IIa}\\ \\ \text{IIb}\end{matrix}\right] \xrightarrow[\text{ROH}]{H_2O_2/KOH} \text{IIa} + \text{IIb} + \underset{\text{(IV)}}{\text{FcCH}{=}\text{CH}{-}\text{C}(\text{CH}_3){=}\text{CH}{-}\text{CONH}_2} \qquad (2)$$

20% 30% 48% for IIa or 39% for IIb

Under similar conditions the *trans*-isomer of β-ferrocenylacrylonitrile trans-

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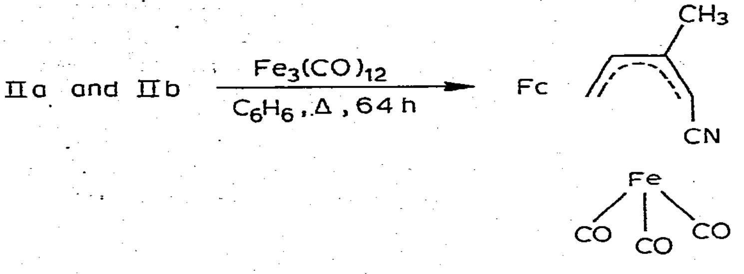
* Detailed experimental data on the chemical separation methods of *cis*- and *trans*-isomers of β-ferrocenylacrylonitrile and on isomerization during Stefen's reaction will be communicated in the near future.

formed entirely into the *trans*-amide, while it was not possible to hydrate the *cis*-isomer [5].

Thus the reactivities of α,β-disubstituted ethylenes and their vinyl analogs, substituted ferrocenylbutadienes, are essentially different.

The mixture of isomers IIa and IIb as well as the pure *cis, trans*-(IIa) and *trans,-trans*-(IIb) were treated with excess $Fe_3(CO)_{12}$ in a Soxhlet apparatus in thiophene-free benzene (eq. 3) (here and elsewhere progress of the reaction was followed by thin layer chromatography on alumina).

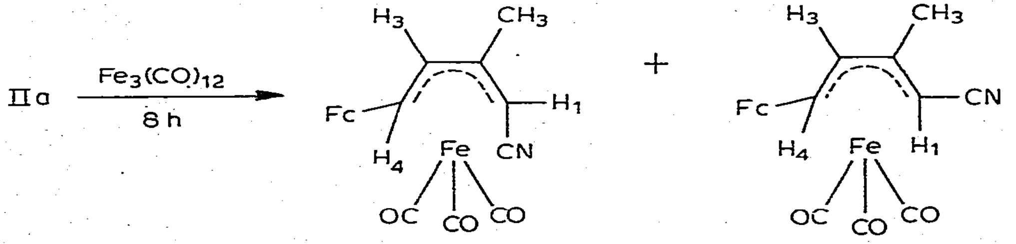


(3)

(IIIa,b) 92 %

It is known that on formation of iron tricarbonyl diene complexes the conjugated diene hydrocarbons transform from *S, trans*- into *S, cis*-configuration. For isomer IIa the present iron tricarbonyl complex, after transition into *S, cis*-configuration, should have the nitrile group in the *anti*-position (IIIa), while for isomer IIb it is in the *cis*-position IIIb. Treatment of IIa with $Fe_3(CO)_{12}$ for 8 h affords the diene complex and unreacted IIa, whereas for IIb the reaction mixture contains a π-complex, IIb and a small amount of IIa.

Analysis of the UV spectra of 1,4-disubstituted buta-1,3-dienes and their corresponding iron tricarbonyl complexes containing ferrocenyl radicals, nitrile and amide groups, and other heterocyclic radicals shows that the ferrocenyl absorption band at 460—500 nm always undergoes a hypsochromic shift (Δλ 24—48 nm). For one derivative, however, no shift was observed for (isomer IIb) while the corresponding IIa derivative showed a shift of 26 nm in this band. These results suggest that compound IIb upon complexation with iron carbonyl may isomerize into IIa, the latter producing a π-complex with an *anti*-located nitrile group (eq. 4).



(IIIa) (IIIb)

(4)

$$\mathrm{IIb} \xrightarrow[8\,h]{Fe_3(CO)_{12}} \mathrm{IIa} \longrightarrow \mathrm{IIIa} + \mathrm{IIIb} \qquad (5)$$

TABLE 3

CHEMICAL SHIFTS (δ ppm) AND SPIN—SPIN COUPLING CONSTANTS (Hz) OF IIIa AND IIIb PROTONS

Compound	H_1	H_3	H_4	CH_3	C_5H_5	C_5H_4	$J(H_3-H_4)$
IIIa	1.88 s	5.51 d	3.61 d	2.13 s	3.96 s	4.04 m	9.5
IIIb	(0.16)	5.43 d	1.99 d	2.42 s	3.96 s	4.08 m	9.5
IIIb [a]	0.16 s	5.14 d	1.73 d	2.09 s	4.03 m		9.5

[a] In C_6D_6.

We roughly separated IIIa from IIIb by means of preparative thin layer chromatography on alumina. Small quantities of the pure compounds were isolated by multiple stepwise crystallization. The IR spectra of IIIa and IIIb were completely identical. Thus to obtain unequivocal evidence of the nitrile group position their PMR spectra were measured.

It should be pointed out TLC and PMR spectral data show that isomer IIIa is the principal component of the mixture. The ratio of isomers IIIa and IIIb is 10/3.

The PMR spectrum of IIIb was measured in CCl_4 using hexamethyldisiloxane (HMDS) as internal standard. The H_1 signal was overlapped by an intense signal from the methyl groups of HMDS so to obtain an accurate H_1 proton chemical shift the spectrum was also taken in CCl_4 in the absence of internal standard with the signal from the five protons of the unsubstituted ferrocenyl ring serving as a reference point. Thus we measured the H_1 chemical shift (δ 0.16 ppm).

The spectrum of compound IIIb was taken in C_6D_6 (Table 3). The C_6H_6 signal due to the impurity in C_6D_6 was used as a reference point (δ 7.27 ppm). According to the H_1 and H_4 proton chemical shifts compound IIIb is the *syn*-isomer. For discussing the PMR spectrum of IIIa the C_5H_5 signal was employed as a reference by assuming that the chemical shifts of C_5H_5 protons in *syn*- and *anti*-isomers are equivalent (3.96 ppm).

The positions of the resonances from H_1 and H_4 protons in the spectrum of IIIa suggest that it is an *anti*-isomer. Compounds IIIa and IIIb do not undergo Pinner or Stefen's reactions nor do they react with CH_3MgI in THF.

Saponification of IIIa and IIIb with 30% ethanolic KOH solution causes decomposition of the complex to give a mixture of the respective amide IV and acid V (eq. 6).

$$\text{IIIa and IIIb} \xrightarrow[C_2H_5OH]{30\%\ KOH} \begin{array}{c} FcCH{=}CH{-}C(CH_3){=}CH{-}CONH_2\ \text{(IV) } 62\% \\ + \\ FcCH{=}CH{-}C(CH_3){=}CH{-}COOH\ \ \text{(V) } 33\% \end{array} \qquad (6)$$

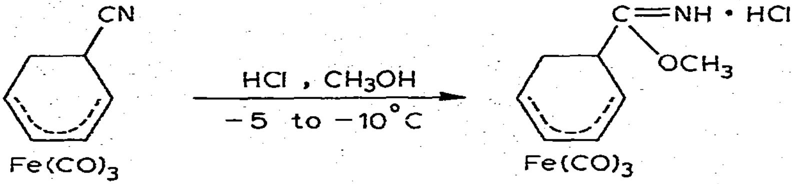
In an analogous manner the mixture of isomers IIa and IIb yielded the same products but in different ratio (eq. 7).

$$\text{IIa and IIb} \xrightarrow[C_2H_5OH]{30\%\ KOH} \text{IV (21\%)} + \text{V (71\%)} \qquad (7)$$

(Cyclohexadieneiron tricarbonyl) carboxylic acid nitriles

No data are available in the literature on the effect of substituent positions in cyclohexa-1,3-dieneiron tricarbonyl complexes upon their reactivity. To attempt to solve this problem the nitrile group was chosen as the substituent. Among the numerous reactions which specify the high polarity of this group and its ready polarizability under the action of different reagents we chose Pinner's reaction which proceeds under mild conditions and usually affords good yields.

Compound 5-CN-h^4-1,2,3,4-$C_6H_7Fe(CO)_3$ (VI) was prepared by the method described in ref. 6. Bubbling dry HCl through an ethereal solution of nitrile VI and excess absolute CH_3OH resulted in the isolation and characterization of (5-cyclohexa-1,3-dienyliron tricarbonyl) carboxylic acid methyl iminoester hydrochloride (VII) (eq. 8).



(8)

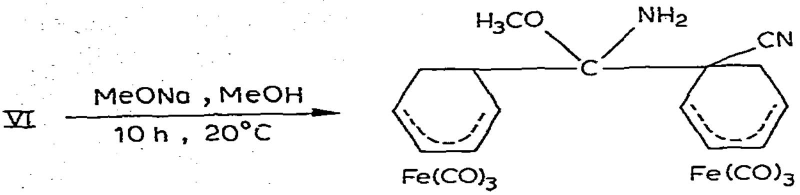
(VI) (VII) 61%

The absence of even traces of the initial nitrile in the reaction products shows that the nitrile group in 5-cyclohexa-1,3-dieneiron tricarbonyl complex is highly active. The comparatively low yield of hydrochloride may be the result of concurrent formation of a π-allylic complex. Special experiments demonstrated that VI only reacts with hydrogen chloride either with formation of the hydrochloride VII or at room temperature. Thus it is unreasonable to increase the yield by using a higher temperature. In this case the π-allylic complex which is generated is unstable and rapidly decomposes into $FeCl_2$. The decomposition products were not investigated.

The structure of the hydrochloride VII obtained was confirmed by reactions specific of this class of compound: thermal decomposition yielded the respective amide of 5-(cyclohexa-1,3-dienyliron tricarbonyl) carboxylic acid (VIIa) (73%) while hydrolysis gave the methyl ester (VIIb) (85%).

To prepare the cyclohexa-1,3-dieneiron tricarbonyl complex with the nitrile group in position 1, we carried out isomerization of VI in the presence of bases as the first step.

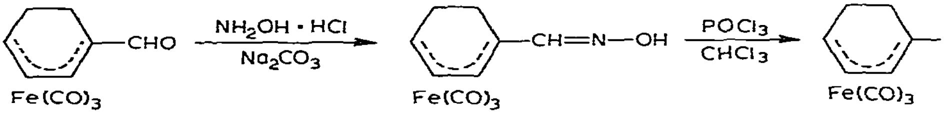
It was shown earlier [7] that refluxing nitrile in an aqueous ethanolic KOH solution gave 1-$CONH_2$-h^4-1,2,3,4-$C_6H_7Fe(CO)_3$ (28%) along with decomposition products. Sodium methylate in methanol was employed as isomerizing agent to prevent hydrolysis of the nitrile group into an amide and to obtain simultaneously a free iminoester. It is important to note that in this case no formation of the free iminoester was observed. This is an effect specific of nitrile groups with highly labile α-hydrogen atoms (cyanoacetic acid ethyl ester) and of nitriles with bulky blocking groups (2-carboethoxy-2-ethylbutyronitrile) [8]. It was unexpectedly found that after stirring the reaction mixture at room temperature for 10 h, a single compound was obtained (m.p. 113—115°C) in low yield together with unreacted VI (33%). Elemental analysis, IR, PMR and mass spectra of this compound allow us to assign it the structure aminomethoxy-(1-cyclohexa-2,4-dienyliron tricarbonyl)-(1′-cyano-1′-cyclohexa-2′,4′-dienyliron tricarbonyl) methane (VIIc) (eq. 9).



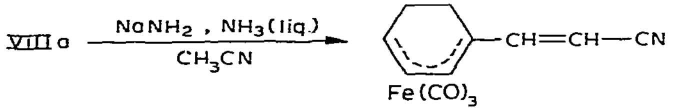
(VIIc) (9)

The formation of aminonitrile VIIc is in agreement with the known fact that hydrogen atoms attached to α-carbons in nitrile compounds possess almost the same acidity as those in the α-positions of carbonyl groups. Thus nitriles undergo addition reactions in a matter analogous to the aldol condensation in the presence of strong bases. In our opinion these results and optimum reaction conditions provide a new opportunity for the synthesis of various derivatives of cyclohexa-1,3-dieneiron tricarbonyl complexes.

1-CN-*h*^{4}-1,2,3,4-$C_6H_7Fe(CO)_3$ (VIII) and β-(1-cyclohexa-1,3-dienyliron tricarbonyl) acrylonitrile (IX) [11] were prepared from the respective aldehyde according to eqs. 10 and 11.



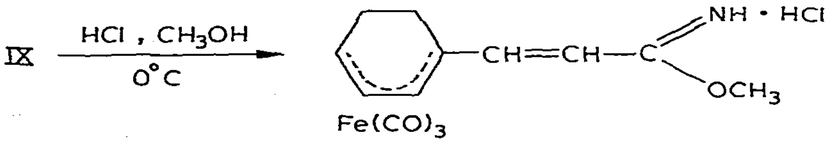
(VIIIa) (VIIIb) (VIII) (10)



(IX) (11)

For compound VIII we failed to perform the reactions specific to the nitrile group: Pinner's reaction and reduction with $LiAlH_4$ to the respective amine.

In the model compound IX the electron density at the C≡N group remains without any significant change. It only shifts from the metal atom to the C=C bond. Under conditions of Pinner's reaction this nitrile affords the respective methyl iminoester hydrochloride X in satisfactory yield (24%) (eq. 12).



(X) (12)

The inertness of the nitrile group in compounds IIIa and VIII may be explained by its participation in the formation of a coordination bond with the metal atom. Since it is known that in reactions of transition metal complexes with α,β-unsaturated compounds containing —COR, —CN, —COOR and —CONH$_2$ groups the π-electrons of these substituents may take part in bond formation with the metal. Moreover the nitrile group may act as a monodentate ligand and produce a bond involving the nitrogen lone electron pair of the cyano group or the C≡N π-electrons. For example three different iron carbonyl complexes containing acrylonitrile were isolated in the photoinduced reaction of Fe(CO)$_5$ and acrylonitrile [9].

The characteristic absorption bands of the —C≡N group in the IR spectra of IIIa and VIII do not shift significantly with respect to those in non-coordinated molecules, i.e. the π-electrons of this group do not participate in bond formation with the iron atom as is confirmed by PMR spectral data and elemental analysis.

The lower polarity of the nitrile group is in agreement with the postulated reduction in electron density in the ligand upon complex formation.

Analysis of the data obtained in this work leads us to the conclusion that steric factors caused by the presence of the iron tricarbonyl fragment are the factors most responsible for the nitrile group reactivity in these π-complexes.

Experimental

IR spectra were taken on a UR-20 spectrophotometer in KBr pellets. PMR spectra were measured on XL-100 Varian and Tesla-80 spectrophotometers in most cases in CCl$_4$ solution. Tetramethylsilane and hexamethyldisiloxane were used as internal standards. The electronic absorption spectra of the prepared compounds were registered in C$_2$H$_5$OH in the region of 200—700 nm on a Specord spectrophotometer with an automatic recording in the concentration range of 10^{-3}—10^{-4} mol l^{-1} at room temperature.

2-Hydroxy-2-methyl-4-ferrocenylbut-3-enecarbonitrile (I)

This compound was prepared from 5.9 g (0.26 mol) of sodium in 250 ml of liquid ammonia, 14.7 g (13.5 ml, 0.064 mol) of acetonitrile and 8.12 g (0.032 mol) of ferrocenalacetone under conditions described elsewhere [2]. 6.6 g (75%) of I were obtained, m.p. 102—103°C (benzene/hexane). Found: N, 4.54. $C_{16}H_{17}$FeNO calcd.: N, 4.74%. IR spectrum: 1600 (C=C), 2260 (C≡N), 3430 cm^{-1} (OH).

2-Methyl-4-ferrocenylbuta-1,3-dienecarbonitrile (IIa,b)

1.5 g (0.01 mol) of POCl$_3$ was added with stirring to a solution of 2.95 g (0.01 mol) of I in 50 ml of dry CHCl$_3$. The mixture was heated to 60—65°C for 30 min. After cooling the reaction mixture was washed with water, 5% carbonate solution, again with water and dried over MgSO$_4$. After removal of the solvent the residue (a mixture of isomers IIa and IIb), 2.6 g (94%), was subjected to thin layer chromatography on alumina (hexane/benzene eluant, 1.25/3). Found for the mixture of IIa and IIb: N, 4.77. $C_{16}H_{15}$FeN calcd.: N, 5.06%. Two isomers were isolated (in order of eluting): 2-*cis*, 4-*trans*- IIa, 0.68 g (26%), m.p. 121—122°C (hexane) and 2-*trans*, 4-*trans*- IIb, 1.92 g (74%), m.p. 130—131°C (hexane). The isomers were identical with the nitriles prepared by dehydration of I in the presence of Fe$_3$(CO)$_{12}$. IR spectrum of IIa or IIb: 1620 (C=C), 2215 cm^{-1} (C≡N).

Action of H_2O_2 in the presence of potassium hydroxide on ethanolic solutions of IIa and IIb

9 ml of a 10% solution of H_2O_2 was slowly added with stirring to a mixture of 0.1 g of IIa or IIb in 10 ml of absolute C_2H_5OH and 0.45 ml of a 50% solution of KOH at 40—45° C. The reaction mixture was stirred for 9 h under heating. The mixture was then cooled, diluted with water and extracted with ether. After evaporation of the solvent the residue was chromatographed on an alumina column. 0.05 g (50%) of isomeric nitriles was eluted with benzene and then separated on a thin layer alumina plate into IIa and IIb. The amide was eluted with a benzene/ethanol mixture. In the former case we obtained: 0.02 g (20%) of IIa, 0.03 g (30%) of IIb and 0.05 g (48.5%) of 2-methyl-4-ferrocenylbuta-1,3-dienecarboxamide (IV), m.p. 170°C (benzene/hexane). The second case yielded: 0.02 g (20%) of IIa, 0.03 g (30%) of IIb and 0.04 g (39%) of IV. Found for IV: C, 65.05; H, 5.92; Fe, 18.73. $C_{16}H_{17}FeNO$ calcd.: C, 65.11; H, 5.80; Fe, 18.92%. IR spectrum: 1600 (C=C), 1620 (NH_2), 1670 (C=O), 3320, 3370, 3470 cm^{-1} (N—H).

1,2,3,4-h^4-2-Methyl-4-ferrocenylbutadienecarbonitrileiron tricarbonyl (IIIa and b)

A solution of 14.3 g (0.052 mol) of a mixture of IIa and IIb in 500 ml of absolute C_6H_6 was placed in a flask equipped with a Soxhlet extractor. 64 g (0.107 mol) of $Fe_3(CO)_{12}$ was placed in Soxhlet thimble. The mixture was stirred for 64 h at 80°C. On completion of the reaction the mixture was filtered and the filtrate evaporated. The residue was recrystallized from heptane. Yield of IIIa and IIIb 92%; m.p. 162—163°C. Found: C, 54.71; H, 3.82; Fe, 26.87; N, 3.43. $C_{19}H_{15}Fe_2NO_3$ calcd.: C, 54.72; H, 3.62; Fe, 26.79; N 3.36%.

Reaction of $Fe_3(CO)_{12}$ with nitrile isomers IIa or IIb

A solution of 0.4 g of $Fe_3(CO)_{12}$ in C_6H_6 heated to 60°C was added slowly with stirring to a solution of 0.1 g of IIa or IIb nitrile isomers in 10 ml of absolute C_6H_6 at 60°C. The mixture was stirred for 8 h under reflux in C_6H_6. After cooling the mixture was filtered, the solvent evaporated and the solids chromatographed on an alumina column. For isomer IIa 0.048 g (32%) of the mixture of complexes IIIa and b and 0.061 g (61%) of unreacted IIa were obtained. For isomer IIb after 6 h, along with the respective IIIa and IIIb, the chromatogram revealed traces of *cis, trans*-isomer IIa which did not increase with time. 0.04 g (27%) of complexes IIIa and IIIb and 0.064 g (64%) of unreacted IIb isomer were obtained.

Action of aqueous KOH on the mixture of isomers IIa and IIb

A mixture of 3.04 g (0.011 mol) of IIa and IIb, 100 ml of C_2H_5OH and 170 ml of 30% KOH solution was refluxed until no more NH_3 was evolved (20 h). During this time 15 g of solid KOH was added. After cooling the mixture was diluted with water and extracted with ether. The ethereal solution was washed with water and dried over $MgSO_4$. After removal of the solvent 0.79 g (21%) of amide IV was obtained, m.p. 170°C. The alkaline solution was acidified with concentrated HCl and the precipitated acid was extracted with ether. The ethereal solution was treated as described above. 2.28 g (71%) of 2-methyl-4-ferrocenylbuta-1,3-dienecarboxylic acid (V) was obtained, m.p. 198°C (dec.) (hexane/benzene).

Found: C, 65.10; H, 5.53; Fe, 18.50. $C_{16}H_{16}FeO_2$ calcd.: C, 64.89; H, 5.45; Fe, 18.86%. IR spectrum: 1290, 1430, 1680, 2500—3000 (COOH), 1600 (C=C) cm^{-1}.

Action of aqueous KOH on 1,2,3,4-h^4-2-methyl-4-ferrocenylbutadienecarbonitrileiron tricarbonyl (IIIa and IIIb)

Saponification was carried out in the same way as for IIa and IIb. 2 g (0.0048 mol) of IIIa and IIIb gave 0.84 g (62%) of IV, m.p. 170°C, and 0.45 g (33%) of V, m.p. 198°C (dec.).

5-(Cyclohexa-1,3-dienyliron tricarbonyl) carboxylic acid methyl iminoester (VII) hydrochloride

Dry HCl was bubbled through a solution of 5 g (0.02 mol) of VI and 1.3 g (1.1 ml, 0.04 mol) of absolute CH_3OH in 25 ml of absolute ether at —5 to —10°C for 40 min. The precipitate was filtered off, washed with absolute ether until neutral reaction and dried under vacuo over alkali. 3.9 g (61%) of VII was obtained, m.p. 100—101°C (dec.) (after repeated precipitation from methanol into ether). Found: Cl, 11.02. $C_{11}H_{12}ClFeO_4N$ calcd.: Cl, 11.19%.

5-(Cyclohexa-1,3-dienyliron tricarbonyl) carboxylic acid amide (VIIa)

1 g (0.0032 mol) of VII was heated on an oil bath for 2 h at 110—115°C. The brown solid which formed was placed in a Soxhlet apparatus and extracted with ether. After removal of the solvent the residue was chromatographed on alumina (benzene/hexane eluant). 0.6 g (73%) of VIIa was obtained, m.p. 116—117°C (benzene/hexane). IR spectrum: 1650 (C=O); 1980, 2070 (C≡O), 3300, 3330, 3470 cm^{-1} (N—H). PMR spectrum: 5.50—5.60 (m, 2, H^2, H^3); 3.20 (m, H^5); 2.98 (m, 2, H^1, H^4); 2.11 (m, 2, H^6, H^6); $J(2,1)$ 3.5 Hz. Found: C, 45.40; H, 3.70; Fe, 21.70. $C_{10}H_9FeNO_4$ calcd.: C, 45.65; H, 3.46; Fe, 21.23%. Mass spectrum, m/e: 263 (M^+), 235 $(M - CO)^+$, 207 $(M - 2\,CO)^+$, 179 $(M - 3\,CO)^+$.

5-(Cyclohexa-1,3-dienyliron tricarbonyl) carboxylic acid methyl ester (VIIb)

25 ml of distilled water was added to a suspension of 1 g (0.0032 mol) of VII in 10 ml of C_6H_6 and stirred at room temperature until the colour of the aqueous layer disappeared. The organic layer was separated off and the aqueous layer was extracted with ether. The organic extracts were combined and dried over magnesium sulfate. After evaporation of the solvent the residue was chromatographed on alumina (benzene eluant). 0.72 g (85%) of VIIb was obtained, b.p. 127—128°C/1.5 mmHg. IR spectrum: 1730 (C=O); 1980, 2070 cm^{-1} (C≡O). Found: C, 47.65; H, 3.74. $C_{11}H_{10}FeO_5$ calcd.: C, 47.51; H, 3.63%.

Aminomethoxy(1-cyclohexa-2,4-dienyliron tricarbonyl)(1'-cyano-1'-cyclohexa-2',4'-dienyliron tricarbonyl)methane (VIIc)

A solution of 3 g (0.0122 mol) of VI was added dropwise with stirring and cooling to 0°C to a solution of 0.53 g (0.0098 mol) of sodium methylate in 20 ml of absolute CH_3OH. The temperature was gradually increased to room temperature and stirring continued for 10 h. The reaction mixture was poured into water and extracted with ether. The organic extracts were combined, washed with water until neutral reaction and dried over $MgSO_4$. After removal of the solvent the residue was chromatographed on alumina. The first fraction gave 1 g

(33%) of the starting nitrile VI, the second fraction yielded 0.3 g (9%) of VIIc (benzene/methanol eluant), m.p. 113—115°C (hexane/benzene). IR spectrum: 1980, 2070 ($C{\equiv}O$), 2250 ($C{\equiv}N$), 3460 (N—H) cm^{-1}. PMR spectrum (pyridine): 4.93 (m, 4, H^2, $H^{2'}$, H^3, $H^{3'}$); 3.17 (s, 1, CH_3); 2.93—2.67 (m, 5, H^1, $H^{1'}$, $H^{4'}$, $H^{5'}$); 193—160 (m, 2, H^6, $H^{6'}$); *J*(6,6) 3; *J*(4,6) 14 Hz. Mass spectrum, *m/e*: 522 (M^+), 492 ($M^+ - CH_2O$). Found: C, 48.40; H, 3.34; Fe, 21.04; N, 5.10. $C_{21}H_{18}Fe_2N_2O_7$ calcd.: C, 48.31; H, 3.48; Fe, 21.39; N, 5.36%.

The complex obtained was a crystalline yellow solid stable in air for long periods, poorly soluble in hydrocarbons, but well-soluble in polar solvents.

1-Formylcyclohexa-1,3-dieneiron tricarbonyl (VIIIa)

This compound was prepared from *N,N*-diethylaminobuta-1,3-diene and acrolein with subsequent treatment by $Fe_3(CO)_{12}$ as described elsewhere [11].

(1-Cyclohexa-1,3-dienyliron tricarbonyl)aldoxime (VIIIb)

2.1 g (0.02 mol) of Na_2CO_3 was slowly added with stirring to a solution of 3.3 g (0.0133 mol) of VIIIa and 1.4 g (0.02 mol) of hydroxylamine hydrochloride in 25 ml of 50% CH_3OH and the mixture stirred for 20 min. The precipitated solid was filtered off, washed with water until neutral reaction and dried in vacuo. 3.14 g (90%) of aldoxime was obtained, m.p. 143—145°C (benzene). Found: C, 45.82; H, 3.29; N, 5.65. $C_{10}H_9FeNO_4$ calcd.: C, 45.66; H, 3.45; N, 5.33%. IR spectrum: 1680 ($C{=}N$); 1990, 2080 ($C{\equiv}O$); 3300 (O—H) cm^{-1}. PMR spectrum: 4.90 (d, 1, H^2); 4.67 (m, 1, H^3); 4.00 (s, 1, OH); 2.80 (m, 1, H^4); 1.03—2.43 (m, 4, H^{5-8}); *J*(2,3) 4 Hz.

(1-Cyclohexa-1,3-dienyliron tricarbonyl) carboxylic acid nitrile (VIII)

A solution of 3 ml (5 g, 0.03 mol) of phosphoryl chloride in 5 ml $CHCl_3$ was added dropwise with stirring to a solution of 1 g (0.0038 mol) of aldoxime (VIIIb) in 20 ml of $CHCl_3$ and the mixture stirred for 4 h at room temperature. The reaction mixture was poured into iced water. The organic layer was separated, washed with water until neutral reaction and dried over $MgSO_4$. After removal of the solvent the residue was chromatographed on alumina (benzene eluant). 0.51 g (55%) of VIII was obtained, m.p. 102—103°C (hexane). Found: C, 49.06; H, 2.93; Fe, 22.83. $C_{10}H_7FeNO_3$ calcd.: C, 49.01; H, 2.89; Fe, 22.79%. IR spectrum: 1980, 2080 ($C{\equiv}O$), 2230 ($C{\equiv}N$) cm^{-1}. PMR spectrum: 5.53 (d, 1, H^2); 5.16 (m, 1, H^3); 3.23 (m, 1, H^4); 1.23—1.90 (m, 2, $H^{5,6}$); *J*(2,3) 4; *J*(3,4) 6 Hz.

Action of $LiAlH_4$ on nitrile VIII

A solution of 2.45 g (0.01 mol) of nitrile VIII was added dropwise (with stirring and cooling with ice) to a suspension of 0.57 g (0.015 mol) of $LiAlH_4$ in 25 ml of absolute ether. The reaction mixture was stirred for 1 h at 0°C and for 2 h at room temperature. The mixture was subjected to the usual treatment and 2.16 g (88%) of the starting nitrile VIII, m.p. 102—103°C, was isolated from the ethereal layer.

Behaviour of VIII under Pinner's reaction conditions

Dry HCl was bubbled for 1 h at —5°C through a solution of 1 g (0.0041 mol) of VIII and 4.96 ml (3.92 g, 0.122 mol) of absolute CH_3OH in 30 ml of absolute ether. The solvent and excess HCl were removed in vacuo and the residue chromatographed to give 0.92 g (92%) of VIII, m.p. 102—103°C.

β-(1-Cyclohexa-1,3-dienyliron tricarbonyl) acrylonitrile (IX)

This compound was obtained as described elsewhere [1]. The data obtained for the nitrile agree with the literature data.

β-(1-Cyclohexa-1,3-dienyliron tricarbonyl) acrylic acid methyliminoester hydrochloride (X)

Dry HCl was bubbled for 4.5 h at 0°C through a solution of 2 g (0.007 mol) of nitrile IX and 8.9 ml (7.18 g, 0.221 mol) of absolute methanol in 60 ml of absolute ether. The precipitated solid was filtered off, washed with ether until neutral reaction and dried over alkali. 0.59 g (24%) of hydrochloride X was obtained, m.p. 94—96° (dec.) (after reprecipitation from methanol into ether). The mass spectrum was measured at 130°C (i.e. when Pinner's rearrangement has already occurred), *m/e*: 261 $(M-CO)^+$, 233 $(M-2\,CO)^+$, 205 $(M-3\,CO)^+$. Found: C, 46.05; H, 4.13; Fe, 16.65; N, 4.20. $C_{13}H_{14}ClFeNO_4$ calcd.: C, 45.98; H, 4.16; Fe, 16.45; N, 4.12%.

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