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# *cis*- AND *trans*-$\beta$-SUBSTITUTED $\alpha$-VINYLFERROCENES. CONFIGURATION OF TRISUBSTITUTED ETHYLENES

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## SUMMARY

A convenient approach to the nitriles of $\alpha$, $\beta$-unsaturated ferrocene carboxylic and 1,1'-ferrocene dicarboxylic acids has been worked out. It involves the condensation of acylferrocenes with acetonitrile and subsequent dehydration of the $\beta$-hydroxynitriles produced. Isomeric unsaturated nitriles were isolated in some cases, and were separated by the thin-layer chromatography. They were found to display substantially different $\alpha(H_{2,5})$proton shieldings in the substituted cyclopentadienyl ring. This phenomenon was used for elucidating the configurations of some $\alpha$-vinylferrocenes triply-substituted at the double bond. Formal redox potentials were determined for $\alpha$-vinylferrocenes containing $NO_2$-, C≡N- and $COCH_3$-groups in the $\beta$-position. These data, together with those of proton magnetic resonance and the $R_f$ values obtained may be employed for the assignment of isomers to the *cis*- or *trans*-series.

## INTRODUCTION

Substituted vinylferrocenes are of interest as the possible monomers for the syntheses of ferrocene-containing polymers. Vinylferrocene[1] as well as certain $\beta$-substituted $\alpha$-vinylferrocenes[2] have been shown to polymerize or enter a copolymerization reaction with other vinyl derivatives. Information on the configuration of the $\beta$-substituted $\alpha$-vinylferrocenes is desirable, since the reactivities of *cis*- and *trans*-ethylenes in the polymerization reaction essentially differ.

In the present study we prepared nitriles of $\alpha$, $\beta$-unsaturated ferrocene carboxylic and 1,1'-ferrocene dicarboxylic acids together with some $\beta$-substituted $\alpha$-vinylferrocenes. Unsaturated ferrocene nitriles were obtained from the corresponding $\beta$-hydroxynitrile ferrocene derivatives.

A convenient route to $\beta$-hydroxynitriles is the reaction of aldehydes and ketones with acetonitrile and its highest derivatives in the presence of alkaline metal amides. Lettré *et al.*[3] were the first to carry out the condensation of benzophenone and other aromatic carbonyl compounds with aceto- and propionitrile. They obtained large yields of $\beta$-hydroxynitriles. Recently this method was used to prepare ferrocene $\beta$-hydroxynitriles[4]; the latter were converted to the previously unknown nitriles of $\alpha$,$\beta$-unsaturated ferrocene carboxylic acids[5].

Unsaturated nitriles obtained in the present study were separated by thin-layer chromatography. Using NMR and IR spectrometry, together with the data of thin-layer chromatography and redox potentials we elucidated the configurations of a series of β-substituted α-vinylferrocenes.

A considerable difficulty was found in the study of the configurations of the triply-substituted ethylenes[6], but a combination of the various methods described enabled unequivocal configurations of some β-substituted α-vinylferrocenes to be obtained in the present work.

Since there is as yet no unequivocal conclusion on the transmittance of electronic effects via the ethylene moiety[7], it seemed reasonable to investigate the effects of substituent on the formal redox potentials of *cis-* and *trans*-substituted α-vinylferrocenes.

## RESULTS

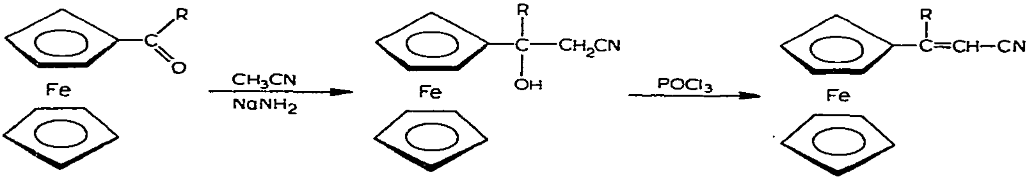
### *Synthesis of β-substituted α-vinylferrocenes*

The majority of α-vinylferrocenes obtained in the present work were prepared via the condensation of acylferrocenes with acetonitrile followed by dehydration of β-hydroxynitriles into the unsaturated nitriles.

Acylferrocenes were reacted with acetonitrile in liquid ammonia in the presence of sodium amide and ethereal or ether–tetrahydrofuran media. The highest yields of β-hydroxynitriles were obtained using two equivalents of sodium amide and acetonitrile per one equivalent of acyl component.

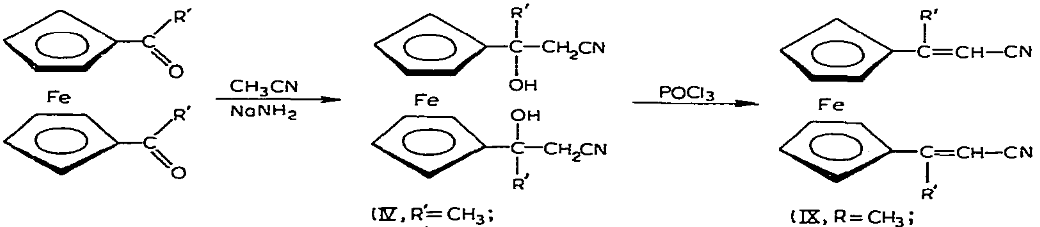
The β-hydroxynitriles obtained are yellow-coloured crystalline substances. Only di-π-(β-cyclopentadienyl-β-hydroxybutyronitrile)iron (IV) was a syrup-like viscous product. The latter was identified *via* the unsaturated dinitrile (IX) which was a crystalline compound (m.p. 132–133°).

Unlike 1,1′-di-(1-hydroxyethyl)ferrocene[8] which dehydrated to the corresponding cyclic ether in the presence of acidic agents, 1,1′-di-β-hydroxynitrile ferrocene derivatives (IV), (V), as well as mono-β-hydroxynitriles (I)–(III) gave quantitati-



(I, R = H;
II, R = CH₃;
III, R = C₆H₅)

(VI a,b, R=H;
VII R=CH₃;
VIII a,b, R=C₆H₅)



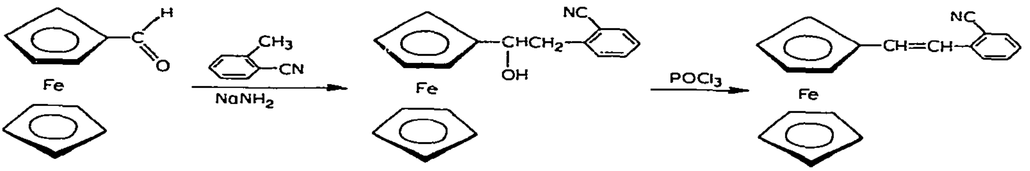
(IV, R′=CH₃;
V, R′=C₆H₅)

(IX, R=CH₃;
X a,b,c, R=C₆H₅)

vely only unsaturated nitriles (VI)–(X). β-Hydroxynitriles were dehydrated by treating the nitrile solution in methylene chloride with phosphoryl chloride.

Thin-layer chromatography on alumina enabled the pure *cis*- and *trans*-isomers of unsaturated nitriles to be isolated. Dehydration of carbinols (II) and (IV) obtained from acetyl- and 1,1'-diacetylferrocene gave only the *trans*- isomers. Other carbinols gave a mixture of the *cis*- and *trans*- isomers in a ratio of ~ 1/2. An investigation of the pure isomers showed that the *cis*-derivatives are less coloured, have lower melting points, better solubilities and larger $R_f$ values than the corresponding *trans*-isomers. Thus, condensation of acylferrocenes with acetonitrile and subsequent dehydration of the resulting β-hydroxynitriles is a convenient procedure for preparing the nitriles of α, β-unsaturated ferrocene carboxylic acids.

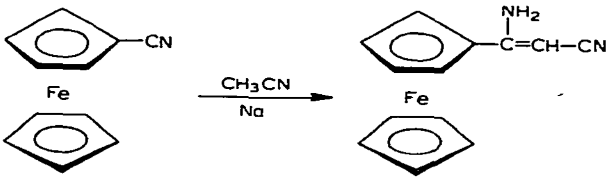
Recently, Hauser *et al.*[9] found that sodium amide in liquid ammonia is an effective ionizing agent for the methyl group of *ortho*- and *para*-toluenenitriles. We carried out the condensation of ferrocenealdehyde with *ortho*-toluenenitrile in the presence of sodium amide in liquid ammonia, and quantitatively dehydrated the hydroxynitrile (XI) obtained to *trans*-β-ferrocenyl-*ortho*-cyanostyrene (XII).



(XI) (XII)

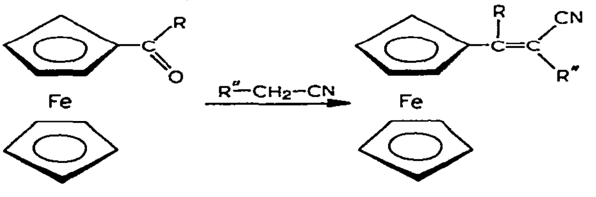
The yields and properties of ferrocenehydroxynitriles (I–V, XI) are shown in Table 1.

β-Ferrocenyl-β-aminoacrylonitrile (XIII) was obtained by the known condensation of nitriles in the presence of metallic sodium[10]. The reaction of cyanoferrocene with acetonitrile was carried out in the presence of sodium powder in hot xylene.



(XIII)

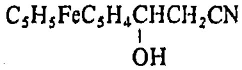
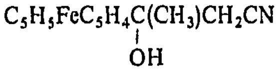
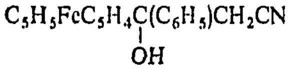
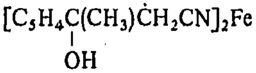
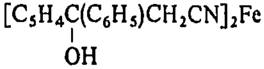
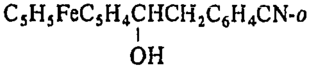
The condensation of ferrocenealdehyde with cyanoacetamide, and malononitrile, and the reaction of acetylferrocene with cyanoacetic ester under the conditions of the Knoevenagel reaction led to β-ferrocenyl-α-cyanoacrylamide (XIV), ferrocenalmalononitrile (XV) and ethyl-β-ferrocenyl-α-cyanocrotonate (XVI), respectively.



(XIV, R=H, R''=$CONH_2$;
XV, R=H, R''=CN;
XVI, R=$CH_3$, R''=$CO_2C_2H_5$)

TABLE 1

PHYSICO-CHEMICAL PROPERTIES OF FERROCENYLHYDROXYNITRILES

| No. | Compound | M.p. (°C) | | $R_f$[a] | Yield (%) | Analysis (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Found | Lit. (ref.) | | | Found | | | | Calcd. | | | |
| | | | | | | C | H | Fe | N | C | H | Fe | N |
| (I) |  $C_5H_5FeC_5H_4\underset{OH}{C}HCH_2CN$ | 108.5–109 | 108.5–109(4) | 0.43 | 85 | 61.23 | 5.12 | 21.80 | 5.41 | 61.18 | 5.10 | 21.90 | 5.48 |
| (II) |  $C_5H_5FeC_5H_4\underset{OH}{C}(CH_3)CH_2CN$ | 110–111 | 110–111(4) | 0.46 | 92 | 64.22 | 5.62 | 20.86 | 5.10 | 63.95 | 5.58 | 20.76 | 5.20 |
| (III) |  $C_5H_5FeC_5H_4\underset{OH}{C}(C_6H_5)CH_2CN$ | 141–142 | 141–142(4) | 0.66 | 95 | 68.75 | 5.25 | 16.83 | 4.45 | 68.75 | 5.14 | 16.87 | 4.23 |
| (IV) |  $[C_5H_4\underset{OH}{C}(CH_3)CH_2CN]_2Fe$ | — | — | 0.21 | 62 | 60.82 | 6.46 | 14.08 | 4.74 | 61.33 | 5.68 | 13.70 | 4.00 |
| (V) |  $[C_5H_4\underset{OH}{C}(C_6H_5)CH_2CN]_2Fe$ | 62–63 | — | 0.29 | 75 | 70.83 | 5.31 | 11.44 | 5.53 | 70.61 | 5.04 | 11.70 | 5.88 |
| (XI) |  $C_5H_5FeC_5H_4\underset{OH}{C}HCH_2C_6H_4CN$-*o* | 118–119 | — | | 68 | 68.63 | 5.33 | 16.76 | | 68.88 | 5.14 | 16.92 | |

[a] Eluent, benzene–ethanol mixture (50 : 1).

Two other vinyl derivatives of ferrocene—ferrocenalacetone (XVII) and β-ferrocenylnitroethylene (XVIII), were earlier prepared by reaction of ferrocenealdehyde with acetone[11] and nitromethane[12].

Table 2 gives the physico-chemical properties of the α-vinylferrocenes prepared. Their structures were confirmed by IR and NMR spectra and elementary analyses.

The IR spectra of unsaturated ferrocenyl nitriles contain, together with bands characteristic of the ferrocene structure also strong absorption of the conjugated C=C (1575–1612 $\text{cm}^{-1}$) and C≡N (2201–2218 $\text{cm}^{-1}$) bonds. Spectra of some α-vinylferrocenes prepared are shown in Fig. 1.

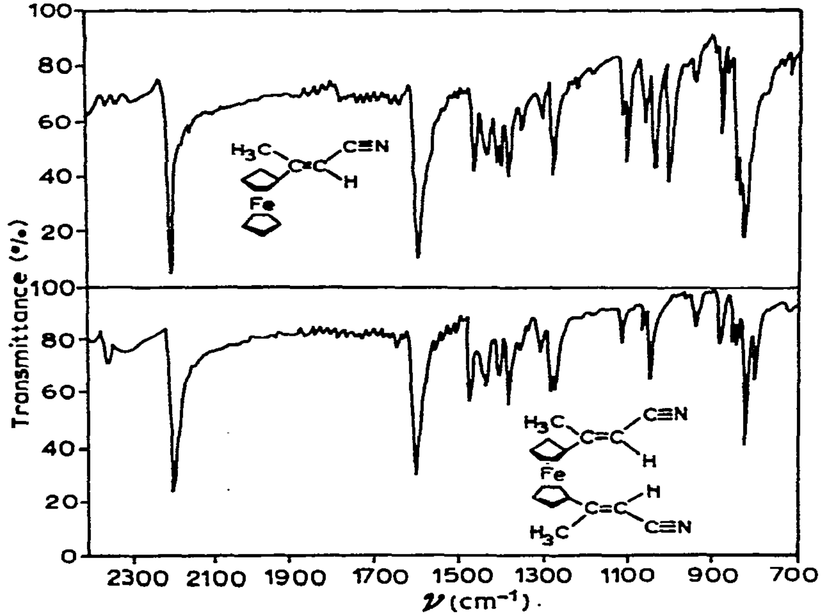


Fig. 1. IR spectra of α-vinylferrocenes (KBr).

β-Ferrocenylacrylonitrile (VIb) shows the band at 963 $\text{cm}^{-1}$ characteristic of the *trans* disubstituted ethylenes; the *cis*-isomer displays no absorption in this region. Moreover, an absorption assigned to the C=C stretching vibration of *cis*-β-ferrocenylacrylonitrile (VIa) is at a lower frequency region (1603 $\text{cm}^{-1}$), than that of *trans*-β-ferrocenylacrylonitrile (1612 $\text{cm}^{-1}$).

No correlation was ever observed for other unsaturated nitriles—trisubstituted ethylene derivatives. We failed to establish the configurations of (VII)–(X) on the basis of the IR spectra alone.

### *NMR spectra of β-substituted α-vinylferrocenes*

The NMR spectral data shown in Table 3 and Fig. 2 also show that the low-melting and high-melting β-ferrocenylacrylonitrile isomers are in *cis* and *trans* configurations: spin–spin coupling constants of the vinyl protons in these compounds are, respectively, 12 and 15 Hz. The four substituted cyclopentadienyl ring protons in *cis*-β-ferrocenylacrylonitrile (VIa) give two triplets at 4.83 and 4.41 ppm: the weak field triplet should be assigned to the $H_{2,5}$ protons, and the strong field triplet to the

TABLE 2

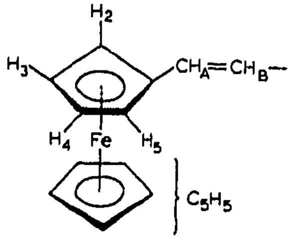
PHYSICO-CHEMICAL PROPERTIES OF $\beta$-SUBSTITUTED $\alpha$-VINYLFERROCENES

| No. | Compound | M.p. (°C) | | $R_f$ | Yield (%) | Analysis (%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Found | Lit. (ref.) | | | Found | | | | Calcd. | | | |
| | | | | | | C | H | Fe | N | C | H | Fe | N |
| (VIa) | $C_5H_5FeC_5H_4CH{=}CHCN$-*cis* | 85–86 | 85–86(5) | 0.77 | ~100 | 65.79 | 5.06 | 23.45 | 6.00 | 65.82 | 4.64 | 23.64 | 5.90 |
| (VIb) | $C_5H_5FeC_5H_4CH{=}CHCN$-*trans* | 93.5–94 | 93.5–94(5) | 0.70 | | 65.85 | 5.02 | 23.48 | 6.00 | 65.82 | 4.64 | 23.64 | 5.90 |
| (VII) | $C_5H_5FeC_5H_4\underset{\mid \atop CH_3}{C}{=}CHCN$-*trans* | 105.5–106 | 105.5–106(5) | 0.68 | ~100 | 66.84 | 5.15 | 21.50 | 5.81 | 66.99 | 5.18 | 21.31 | 5.58 |
| (VIIIa) | $C_5H_5FeC_5H_4\underset{\mid \atop C_6H_5}{C}{=}CHCN$-*cis* | 69.5–70 | 69.5–70(5) | 0.79 | ~100 | 72.65 | 5.18 | 18.13 | 4.70 | 72.84 | 4.79 | 17.90 | 4.47 |
| (VIIIb) | $C_5H_5FeC_5H_4\underset{\mid \atop C_6H_5}{C}{=}CHCN$-*trans* | 99–100 | 99–100(5) | 0.64 | | 72.71 | 5.22 | 18.06 | 4.48 | 72.84 | 4.79 | 17.90 | 4.47 |
| (IX) | $[C_5H_4\underset{\mid \atop CH_3}{C}{=}CHCN]_2Fe$-*trans,trans* | 132–133 | — | 0.27 | ~100 | 68.29 | 5.16 | 17.50 | 8.75 | 68.36 | 5.06 | 17.62 | 8.86 |
| (Xa) | $[C_5H_4\underset{\mid \atop C_6H_5}{C}{=}CHCN]_2Fe$-*cis,cis* | 123–124 | — | 0.57 | ~100 | 76.48 | 4.80 | 12.63 | 6.35 | 76.40 | 4.55 | 12.70 | 6.35 |
| (Xb) | $[C_5H_4\underset{\mid \atop C_6H_5}{C}{=}CHCN]_2Fe$-*cis,trans* | 42–44 | — | 0.48 | | 76.52 | 4.90 | 12.62 | 6.40 | 76.40 | 4.55 | 12.70 | 6.35 |
| (Xc) | $[C_5H_4\underset{\mid \atop C_6H_5}{C}{=}CHCN]_2Fe$-*trans,trans* | 161–162 | — | 0.25 | | 76.45 | 4.72 | 12.64 | 6.18 | 76.40 | 4.55 | 12.70 | 6.35 |
| (XII) | $C_5H_5FeC_5H_4CH{=}CHC_6H_4CN$-*o-trans* | 140–141 | — | | ~100 | 72.59 | 4.84 | 17.54 | | 72.81 | 4.79 | 17.88 | |
| (XIII) | $C_5H_5FeC_5H_4\underset{\mid \atop NH_2}{C}{=}CHCN$ | 163.5–164 | — | 0.45[a] | 35 | 61.90 | 4.77 | 22.22 | 11.11 | 61.77 | 4.78 | 22.0 | 11.25 |
| (XIV) | $C_5H_5FeC_5H_4CH{=}C(CN)CONH_2$ | 142–143 | — | 0.22[a] | 95 | 54.31 | 4.28 | 19.52 | 10.10 | 54.13 | 4.13 | 19.44 | 9.70 |
| (XV) | $C_5H_5FeC_5H_4CH{=}C(CN)_2$ | 100–101 | — | 0.60 | ~100 | 64.20 | 3.85 | 21.54 | 11.02 | 64.12 | 3.81 | 21.37 | 10.70 |
| (XVI) | $C_5H_5FeC_5H_4C(CH_3){=}C(CN)CO_2C_2H_5$ | 101–101.5 | — | 0.61 | 73 | 62.94 | 5.64 | 17.79 | 4.15 | 63.16 | 5.57 | 17.34 | 4.33 |
| (XVII) | $C_5H_5FeC_5H_4CH{=}CHCOCH_3$ | 79–80 | 79–80(11) | 0.42 | 85 | 66.26 | 5.45 | 22.25 | — | 66.20 | 5.52 | 22.02 | — |
| (XVIII) | $C_5H_5FeC_5H_4CH{=}CHNO_2$ | 139–140 | 139–140(12) | 0.73 | 76 | 56.22 | 4.59 | 21.59 | 5.56 | 56.00 | 5.28 | 21.80 | 5.45 |

[a] Eluent, benzene-ethanol mixture (50/1).

TABLE 3

NMR SPECTRA OF β-SUBSTITUTED α-VINYLFERROCENES[a]



| No. | Compound | Chemical shift and multiplicity[b] | | | | | | | Spin-spin coupling const. $J$(AB) (Hz) |
|---|---|---|---|---|---|---|---|---|---|
| | | $C_5H_5$ | $H_{2,5}$ | $H_{3,4}$ | $H_A$ | $H_B$ | $CH_3$ | $C_6H_5$ | |
| (VIa) | $C_5H_5FeC_5H_4CH$=CHCN-*cis* | 4.16 s | 4.83 t | 4.41 t | 6.82 d | 5.17 d | | | 12 |
| (VIb) | $C_5H_5FeC_5H_4CH$=CHCN-*trans* | 4.17 s | 4.42 s | 4.42 s | 7.22 d | 5.43 d | | | 15 |
| (VII) | $C_5H_5FeC_5H_4\underset{\underset{\displaystyle CH_3}{\vert}}{C}$=CHCN-*trans* | 4.11 s | 4.42 m | 4.34 m | | 5.29 q | 2.32 d | | |
| (VIIIa) | $C_5H_5FeC_5H_4\underset{\underset{\displaystyle C_6H_5}{\vert}}{C}$=CHCN-*cis* | 4.18 s | 4.82 t | 4.41 t | | 5.16 s | | 7.31 s | |
| (VIIIb) | $C_5H_5FeC_5H_5\underset{\underset{\displaystyle C_6H_5}{\vert}}{C}$=CHCN-*trans* | 4.12 s | 4.24 s | 4.24 s | | 5.59 s | | 7.43 s | |
| (XII) | $C_5H_5FeC_5H_4CH$=$CHC_6H_4CN$-*o-trans* | 4.10 s | 4.47 t | 4.27 t | 7.00 s | 7.00 s | | 7.38 m | |
| (XVII) | $C_5H_5FeC_5H_4CH$=$CHCOCH_3$-*trans* | 4.15 s | 4.48 m | 4.38 m | 7.83 d | 6.33 d | 2.22 s | | 16 |
| (XVIII) | $C_5H_5FeC_5H_4CH$=$CHNO_2$-*trans* | 4.29 s | 4.89 m | 4.66 m | 8.05 d | 7.49 d | | | 13.5 |
| (XV) | $C_5H_5FeC_5H_4CH$=$C(CN)_2$ | 4.31 s | 4.96 t | 4.74 t | 7.60 s | | | | |

[a] Spectra of all compounds were taken in $CCl_4$ except the spectrum of (XVIII) measured in acetone. [b] δ Scale is used (ppm); accuracy of measurement ±0.02 ppm. s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet.

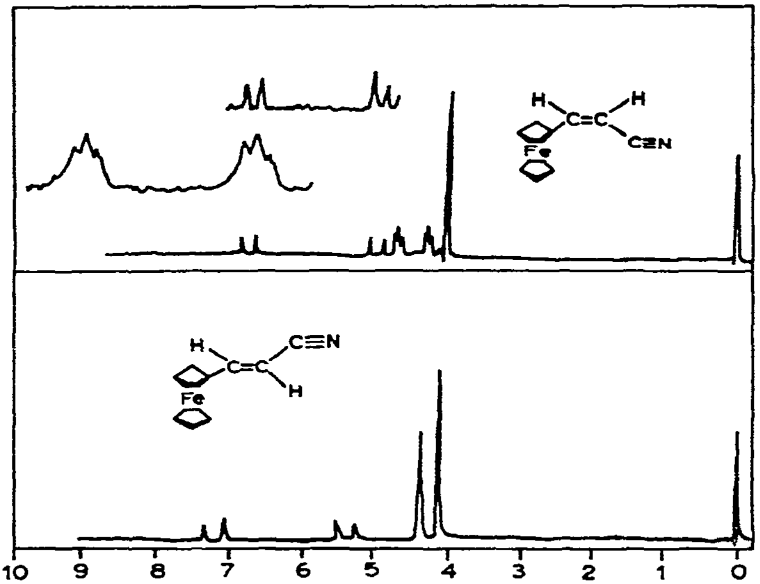


Fig. 2. NMR spectra of *cis*- and *trans*-β-ferrocenylacrylonitriles.

$H_{3,4}$ protons. This signal assignment was based on the results of Rausch and Siegel[13] by comparing the spectra of vinylferrocene and 2,5-dideuterovinylferrocene. In the general case, the cyclopentadienyl ring protons in (VIa), as well as in all the α-vinylferrocenes investigated in this work, give signals shifted down-field with respect to that of ferrocene itself (4.04 ppm in $CCl_4$).

Unlike the *cis*-isomer (VIa), the four substituted ring protons of *trans*-β-ferrocenylacrylonitrile (VIb) give a narrow signal at 4.42 ppm.

All isomers that were assigned to the *trans* series give similar spectra: the $H_{2,5}$ proton signal of the *trans*-isomers is shifted upfield, usually imposing on the $H_{3,4}$ signal*. The low-melting isomer of β-ferrocenylcinnamonitrile (VIIIa) displays the $H_{2,5}$ and $H_{3,4}$ proton signals at 4.82 and 4.41 ppm, respectively, while in the spectrum of the high-melting isomer (VIIb) all four substituted ring proton signals give a wide signal at 4.41 ppm.

β-Ferrocenylcrotonitrile (VII) shows a singlet from the five unsubstituted ring protons and a multiplet from the protons of the substituted ring centered at 4.38 ppm; the methyl and vinyl protons give a doublet and quadruplet at 2.32 and 5.29 ppm, respectively.

From the results obtained it is concluded that compounds (VIa) and (VIIIa) have *cis*-, and (VIb) and (VII) and (VIIIb) have *trans* configurations. A comparison of the physical properties of the isomeric pairs, (VIa) and (VIb) and (VIIIa) and (VIIIb), shows that the *cis*-isomers are less coloured, have lower melting points and larger $R_f$ values than the corresponding *trans*-isomers.

The dependences observed were used for establishing the configurations of

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* The four substituted ring protons of β-ferrocenyl-*ortho*-cyanostyrene give two close triplets at 4.47 and 4.27 ppm.

nitriles (Xa, b, c). Isomeric nitriles (Xa), (Xb) and (Xc), may be arranged in a series of decreasing $R_f$ values but compound (Xa) has a lower melting point than (Xc). Of all three isomers, dinitrile (Xb) with an intermediate $R_f$ value has the lowest melting point. These data indicate that the isomeric dinitriles (Xa), (Xb) and (Xc) should be in *cis-cis*, *cis-trans* and *trans-trans* configurations, respectively. The low melting point (42–44°) of isomer (Xb) with respect to those of (Xa) and (Xc) may be a result of its unsymmetrical structure.

In the spectrum of *cis,cis*-di-π-(β-cyclopentadienylcinnamonitrile)iron (Xa) there are two triplets at 4.52 and 4.73 ppm from the $H_{3,4}$ and $H_{2,5}$ protons, respectively, and also singlets from the vinyl (5.21 ppm) and phenyl protons (7.25 ppm). These signal intensities are in the ratio: 2/2/1/5. In the spectrum of the *cis-trans* isomer (Xb) of the same compound the phenyl protons give two maxima at 7.32 ppm as the proton signals of the unequivalent benzene rings impose. Unlike the *cis-cis* isomer, the vinyl protons are also unequivalent displaying signals at 5.57 and 5.34 ppm. A comparison with the spectra of isomeric β-ferrocenylcinnamonitriles (VIIIa, b) resolves their signal assignment: a weak field signal should be assigned to the *trans*, and a strong field signal to the *cis* fragments of the molecule. The protons of the cyclopentadienyl ring located in the *trans*-position to the nitrile group give two triplets centered at 4.82 ($H_{2,5}$) and 4.47 ppm ($H_{3,4}$). The *trans*-positioned cyclopentadienyl ring shows a singlet at 4.38 ppm.

The spectrum of *trans*, *trans*-di-π-(β-cyclopentadienylcinnamonitrile)iron (Xc) taken in acetonitrile shows a singlet from the phenyl protons at 6.63 ppm, a singlet from the vinyl protons at 5.05 ppm and a multiplet centered at 3.63 ppm, with intensities in the ratio 5/1/4, respectively.

Di-π-(β-cyclopentadienylcrotonitrile)iron (IX) which, as in case of (VII), is produced as a single isomer having identical substituents at the double bond exists probably in its *trans-trans* configuration*.

### *Redox potentials of β-substituted α-vinylferrocenes*

Earlier[14] it was shown that the majority of ferrocene derivatives can readily be titrated with potassium dichromate in a mixture of acetic and perchloric acids. Thus enabling their redox potentials to be determined. Depending on the nature of the substituents, the potential values vary considerably. The electron-releasing (with respect to ferrocene) substituents usually decrease, and the electron-withdrawing substituents increase the redox potentials with respect to unsubstituted ferrocene. The redox potentials of seven vinylferrocene derivatives obtained in the present work are shown in Table 4. All the vinyl derivatives gave redox curves typical of reversible systems. As can be seen from the data of Table 4, of the seven vinylferrocenes investigated, vinylketone (XVII) has the lowest (−0.403 V) and nitroethylene (XVIII) the highest (−0.487 V) potentials. Unsaturated nitriles (VIa, b), (VII) and (VIIIa, b) show intermediate values. *trans*-Disubstituted ethylenes, (XVIII), (VIb) and (XVII), may thus be arranged in the following series of decreasing redox potentials: $C_5H_5FeC_5H_4CH{=}CHNO_2 > C_5H_5FeC_5H_4CH{=}CHCN > C_5H_5FeC_5H_4CH{=}CHCOCH_3$. On going from (XVIII) to (VIb) and further to (XVII), the out-of-plane CH=CH bond

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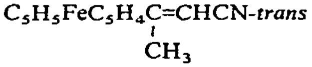
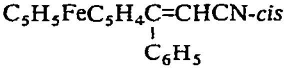
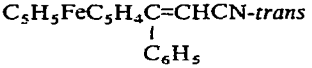
* Ferrocenalmalononitrile (XV) shows a singlet from the vinyl proton (7.60 ppm), two triplets from the $H_{2,5}$ and $H_{3,5}$ substituted ring protons (4.96 and 4.74 ppm) and an unsubstituted ring proton signal (4.31 ppm).

TABLE 4

FORMAL REDOX POTENTIALS OF $\beta$-SUBSTITUTED $\alpha$-VINYLFERROCENES

| No. | Compound | M.p. (°C) | $E_{f_0}$ (V) *vs.* SCE[a] |
|---|---|---|---|
| (VIa) | $C_5H_5FeC_5H_4CH{=}CHCN$-*cis* | 85–86 | −0.436 |
| (VIb) | $C_5H_5FeC_5H_4CH{=}CHCN$-*trans* | 93.5–94 | −0.430 |
| (VII) |  $C_5H_5FeC_5H_4\underset{CH_3}{C}{=}CHCN$-*trans* | 105.5–106 | −0.427 |
| (VIIIa) |  $C_5H_5FeC_5H_4\underset{C_6H_5}{C}{=}CHCN$-*cis* | 69.5–70 | −0.454 |
| (VIIIb) |  $C_5H_5FeC_5H_4\underset{C_6H_5}{C}{=}CHCN$-*trans* | 99–100 | −0.450 |
| (XVII) | $C_5H_5FeC_5H_4CH{=}CHCOCH_3$-*trans* | 79–80 | −0.403 |
| (XVIII) | $C_5H_5FeC_5H_4CH{=}CHNO_2$-*trans* | 139–140 | −0.487 |

[a] Average deviation does not exceed 0.003 V.

vibrations and the spin–spin coupling constants of the vinyl protons were found to increase in the same sequence. Recently[15], the spin–spin coupling constants of the ethylene protons of a large number of 1,2-substituted ethylenes have been shown to decrease with increasing electronegativity of the substituents at the double bond.

Replacement of the $\beta$-vinyl proton in *trans*-$\beta$-ferrocenylacrylonitrile (VIb) with the methyl group (compound VII) decreases (−0.427 V), while the phenyl group (compound VIIIb) increases (−0.450 V), the potential value with respect to that of the starting nitrile (−0.430 V).

On comparison of the *cis*- and *trans*-forms of $\beta$-ferrocenylacrylonitrile with those of $\beta$-ferrocenylcinnamonitrile, it can be seen that the *cis*-isomers have higher potentials (*i.e.*, they are somewhat more difficult to oxidize) than the corresponding *trans*-isomers.

This may be of use, along with other methods, for making isomer assignments to the *cis*- or *trans*-series.

## DISCUSSION

A combination of the methods discussed enables the configurations of disubstituted $\alpha$-vinylferrocenes to be unequivocally established. Moreover, the specificity of the NMR spectra, the change of redox potentials and the chromatographic behaviour make it possible to assign the isomeric ethylenes obtained in the present study to the *cis*- or *trans*-series.

The characteristics outlined deserve more detailed discussion. It is known that the electron-withdrawing substituents in the ferrocene derivatives exhibit substantially different effects on the shielding of $\alpha$ and $\beta$ protons giving two triplets in accord with the *AA′BB′* system. This is in agreement with our results obtained for the *cis*-isomers: the spectra show two triplets in the down-field region with respect to the unsubstituted ring proton signal. These are separated by ~0.4 ppm. On comparing the chemical shifts (Table 5) it can be seen that either a *cis*-vinylene moiety inserted between the ferrocenyl and nitrile groups or (analogously) the introduction of the nitrile into the *cis*-position of vinylferrocene leads to regular changes of chemical shift

TABLE 5

RING PROTON CHEMICAL SHIFTS OF THE MONO-SUBSTITUTED FERROCENE DERIVATIVES $C_5H_5FeC_5H_4$–X (PPM)
Spectra of compounds 1–6 were taken in $CCl_4$, the spectrum of compound 7, in acetone. Data on vinylferrocene (2) are taken from ref. 17, for cyanoferrocene (3) from ref. 16. Chemical shifts are quoted on the δ-scale with respect to the proton signals in $(CH_3)_4Si$, $\Delta C_5H_5$, $\Delta H_{2,5}$, and $\Delta H_{3,4}$ are the chemical shifts of the unsubstituted ring protons, $H_{2,5}$ and $H_{3,4}$ the proton chemical shifts with respect to those in unsubstituted ferrocene.

| No. | –X | $C_5H_5$ | $H_{2,5}$ | $H_{3,4}$ | $\Delta C_5H_5$ | $\Delta H_{2,5}$ | $\Delta H_{3,4}$ |
|---|---|---|---|---|---|---|---|
| 1 | –H | 4.04 | — | — | 0.00 | 0.00 | 0.00 |
| 2 | $-CH{=}CH_2$ | 3.97 | 5.06 | 4.22 | +0.07 | −1.02 | −0.18 |
| 3 | –CN | 4.27 | 4.57 | 4.28 | −0.23 | −0.53 | −0.24 |
| 4 | –CH=CH–CN<br>*cis* | 4.16 | 4.83 | 4.41 | −0.12 | −0.78 | −0.37 |
| 5 | –CH=CH–CN<br>*trans* | 4.17 | 4.42 | 4.42 | −0.13 | −0.38 | −0.38 |
| 6 | $-CH{=}CH{-}COCH_3$<br>*trans* | 4.15 | 4.48 | 4.38 | −0.11 | −0.44 | −0.34 |
| 7 | $-CH{=}CH{-}NO_2$<br>*trans* | 4.29 | 4.89 | 4.66 | −0.25 | −0.85 | −0.62 |

which are caused by the usual substituent effects: the proton chemical shifts for the unsubstituted ring vary in accord with the changing inductive effects of the substituents[16] in the series: $CH{=}CH_2 <$ *cis*-CH=CH–CN < CN; the signal positions of the substituted ring protons depend upon inductive as well as (mainly) the resonance effects of substituents changing in the sequence: *cis*-CH=CH–CN > CN > $CH{=}CH_2$. Unlike $H_{3,4}$, the $H_{2,5}$ protons are more sensitive to the change in substituent effects.

In the spectra of the *trans*-isomers of β-substituted α-vinylferrocenes, the unsubstituted ring proton chemical shifts increase with respect to those in ferrocene itself with increasing electron-withdrawing effects of the substituents ($COCH_3$, −0.11; C≡N, −0.13; $NO_2$, −0.25) and are almost equivalent to those of the corresponding *cis*-isomers (when there are such isomers). This testifies to the inductive nature of the electronic effects in *trans*-isomers. The spectral behaviour of the substituted ring protons in *trans*-isomers is unusual.

On going from *cis*- to *trans*-isomers the $H_{2,5}$ proton signals probably shift up-field. Hence, the four substituted cyclopentadienyl ring protons produce a complex multiplet, or as in the case of *trans*-β-ferrocenylacrylonitrile (Fig. 2), a narrow signal.

There is no ready explanation of this phenomenon in the metallocene series, and an additional detailed study will perhaps be required. It may be noted, however, that the effect observed cannot be explained by a simple change of magnetic anisotropy of the substituent attached to the ferrocene nucleus.

There is a certain inconsistence with traditional concepts in the results describing the substituent effects in *cis*- and *trans*-positions upon the redox potentials. However, it is difficult to draw sound conclusions on the different transmittance of the electronic effects in the *cis*- and *trans*-substituted α-vinylferrocenes, when dealing with only a few examples and a negligible potential difference for the two isomers.

## EXPERIMENTAL

The NMR spectra of the compounds prepared were taken on a Perkin–Elmer R-12 spectrometer at an operating frequency of 60 mHz. Infrared spectra were recorded on an UR-10 spectrometer. Samples were pelletized with KBr. Melting points were determined in a capillary. "Aluminii okis' bezvodnaya" ("anhydrous" aluminum oxide) was employed for thin-layer chromatography of the ferrocene derivatives.

### *Ferrocenylhydroxynitriles (I)–(V), (XI)*

The following general procedure was used for the syntheses of hydroxynitriles: To a suspension of 0.06 mole of sodium amide in liquid ammonia (150 ml) was added 0.06 mole of acetonitrile in 10 ml of absolute ether with vigorous stirring. After 5 min, 0.03 mole of acylferrocene (or 0.015 mole of 1,1′-diacylferrocene) in ether or ether–tetrahydrofuran (1/4) mixture was added rapidly, dropwise. Acylferrocenes were reacted for 5–10 min, diacylferrocenes for 40–60 min. The mixture was then neutralized with an excess of ammonium chloride solution in liquid ammonia, the latter evaporated and the residue treated with water. The ethereal layer was separated from the aqueous layer and the latter exhaustively extracted with ether. The combined ethereal solutions were washed with water, dried over $Na_2SO_4$ and the solvent evaporated. Depending on the yield of hydroxynitrile (see Table 1) the residue was recrystallized from n-hexane–methylene chloride mixture (3/1) or purified from unreacted acylferrocene by chromatography on alumina. The yields and properties of the hydroxynitriles obtained (I)–(V), (XI) are shown in Table 1.

### *Dehydration of hydroxynitriles to unsaturated nitriles (VI)–(X), (XII)*

To a solution of 0.01 mole of hydroxynitrile (I)–(V), (XI) in 15 ml of methylene chloride was added 0.002 mole of phosphoryl chloride, and the red solution resulting heated for 20 min. After cooling, the reaction mixture was washed successively with water, 5% carbonate solution and water, and then dried over $Na_2SO_4$. After evaporation of the solvent, the corresponding nitrile (VI)–(X), (XII) was obtained in almost quantitative yield. The yields and properties of the unsaturated nitriles prepared are shown in Table 2.

*β′-Ferrocenyl-β-aminoacrylonitrile (XIII)*, 2.85 (0.013 mole) of cyanoferrocene and 1.1 g (0.026 mole) of acetonitrile in 20 ml of xylene were added dropwise to a suspension of 0.52 g (0.026 mole) of sodium in 15 ml of xylene for 60 min with stirring and heating on a silicon bath to 100–105°. The stirring and heating were continued for 4 h. After cooling, the solid was filtered off and washed with ether. The benzene suspension of the precipitate was treated with cold water. The benzene layer was separated and dried over $Na_2SO_4$. The solvent was evaporated and the residue recrystallized from benzene. 1.15 g (35%) of β-ferrocenyl-β-aminoacrylonitrile was obtained in a form of red-brown crystals, m.p. 163.5–164° (in sealed capillary).

*β′-Ferrocenyl-α-cyanoacryloamide (XIV)*. To 2.14 g (0.01 mole) of ferrocenaldehyde and 0.83 g (0.01 mole) of cyanoacetamide in 80 ml of absolute methanol were added several drops of piperidine, and the mixture refluxed for 2 h. The methanol was evaporated to ~20 ml and 100 ml of water was added. The solid precipitated was extracted with chloroform. After evaporation of the solvent the mixture was recrystallized from ethanol. 2.65 g (95%) of a violet-red product was obtained, m.p. 142–143°.

*Ferrocenalmalononitrile (XV)*. This was prepared under the same conditions as (XIV) from 10.7 g of ferrocenaldehyde and 3.3 g of malononitrile. 12.7 g (~ 100%) of a dark violet product was obtained, m.p. 100–101° (from n-heptane).

*Ethyl-β-ferrocenyl-α-cyanocrotonate* (*XVI*). 4.56 g (0.02 mole) of acetylferrocene, 2 ml of cyanoacetic ester, 20 ml of glacial acetic acid and 100 ml of benzene were placed in a flask fitted with a reflux condenser and a Dine–Stark trap. The mixture was heated on a water bath for 8 h with the addition of 0.4 g of ammonium acetate in small portions.

After cooling, the reaction mixture was washed with water and dried over $MgSO_4$. After evaporation of the solvent, the residue was chromatographed on an alumina column. 4.7 g (73%) of ethyl $\beta$-ferrocenyl-$\alpha$-cyanocrotonate was eluted with benzene. Red-violet crystals, m.p. 101–101.5° (from n-hexane) were obtained.

*Ferrocenalacetone* (*XVII*). This was obtained using a procedure already described[12] in 85% yield, m.p. 79–80° (lit.[12] 79–80°).

*β-Ferrocenylnitroethylene* (*XVIII*). To sodium methylate (prepared by dissolving 1.38 g (0.06 mole) of metallic sodium in 40 ml of absolute methanol) was added 200 ml of dry ether. To the suspension of sodium methylate obtained were added dropwise 6.42 g (0.03 mole) of ferrocenaldehyde and 3.4 ml (0.06 mole) of nitromethane in 150 ml of ether with vigorous stirring. The reaction mixture was stirred for 2 h and the resulting light yellow residue filtered on a glass filter, washed with ether and treated with 10% hydrochloric acid. The dark violet solid precipitated was extracted with ether, dried over $MgSO_4$ and the solvent evaporated. 5.7 g (76%) of $\beta$-ferrocenylnitroethylene was obtained. Recrystallization from a 3/1 mixture of n-hexane – methylene chloride gave dark violet needles, m.p. 139–140° (lit.[13] 139–140°).

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