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Preliminary communication

Protophilic isotopic hydrogen exchange of 1-ferrocenyl-2-(nitrophenyl)ethylenes

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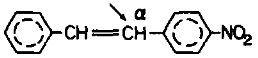
Abstract

cis-1-Ferrocenyl-2-(4-nitrophenyl)ethylene enters into the protium/deuterium exchange in basic medium at the expense of hydrogens of the phenyl ring, at *ortho* positions in respect of the nitro group. The homoaromatic analogue, 4-nitrostilbene, under the same conditions, undergoes isotopic exchange occurring exclusively at the vinylic CH fragment attached to the nitrophenyl group. The difference is eliminated as a result of the shift of the nitro group from position 4 into position 2 of the phenyl ring: *cis*-1-ferrocenyl-2-(2-nitrophenyl)ethylene enters into H^+/D^+ exchange in the same manner as 4-nitrostilbene.

1-Ferrocenyl-2-(nitrophenyl)ethylene contains an ethylenic bond which is simultaneously affected by the acceptor substituent NO_2 ($\sigma_p = 0.78$) and the donor Fc ($\sigma_p = -0.18$). The push-pull effect can operate and, as a result, can lead to large hyperpolarizability. For instance, 1-ferrocenyl-2-(4-nitrophenyl)ethylene has large non-linear optical properties; the compound provides highly efficient second harmonic generation [1].

The electronic properties of the molecules can be manifested by the acidity of different CH bonds and can be studied by means of protophilic isotopic hydrogen exchange (PIHE).

In this short communication, the direction of PIHE has been analysed for 4-nitrostilbene (**1**), 1-ferrocenyl-2-(nitrophenyl)ethylenes (**2–4**) in comparison with 1-ferrocenyl-2-phenylethylene (**5**), 4-nitroaniline (**6**) and nitrobenzene (**7**).



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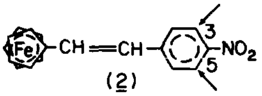

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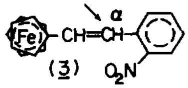

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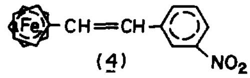

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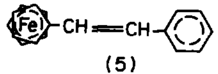

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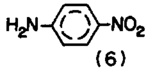
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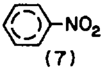
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Table 1

Protophilic isotopic hydrogen exchange (PIHE) of compounds **1–3**; conditions are: ^{t}BuOD/THF(1:1), ^{t}BuOK, 50°C, 4-h exposure (or 25 h with the same results); the conditions used are similar to those in [2]

Initial compound	Isolated product [a]		*cis*/*trans* conversion (%)
	Position of D	Depth of D insertion (%)	
cis-**1** [b]	α	80	49
trans-**1** [b]	α	10	0.2
cis-**2**	3 and 5	30	27
trans-**2**	3 and 5	7	0
cis-**3**	α	100 [c]	0
trans-**3**	None	0	0

[a] Isolation was performed by means of TLC, position of D and D enrichment were found from the PMR spectra. [b] According to the data in [3]. [c] See text.

The arrows show the direction of the reaction if it takes place. The main conditions of PIHE (strictly constant for the substances mentioned) are indicated in Table 1.

Compounds **4**, **5** (*cis* or *trans*) and **6**, **7** do not enter into PIHE under these conditions.

The conclusion about quantitative deuteration was based on the PMR spectrum of the deuterated *cis*-**3**; the accuracy of this method was about 5%. For that reason, the IR spectra of the solid *cis*-**3** and its deutero derivative were compared. The band ν(C=C) 1632 cm^{-1} in the IR spectrum of the initial *cis*-**3** shifts to 1614 cm^{-1} in the IR spectrum of the deutero analogue. Such a shift is typical of monodeutero derivatives $R^1CH{=}CDR^2$; for bis(deutero)derivatives, $R^1CD{=}CDR^2$, this shift is more significant (50–60 cm^{-1}). The bands of symmetric and antisymmetric valent vibrations of the nitro group in the spectrum of *cis*-**3** at 1523 and 1348 cm^{-1} shift, as a result of deuteration, to 1516 and 1343 cm^{-1}, respectively. This attests to deuteration of the benzene ring. In addition, the participation of the benzene ring in deuteration is visualized through the changes in the spectral region of 770–700 cm^{-1}, where the band of non-planar deformation vibrations ρ(CH) of the *ortho* substituted benzene ring are usually observed. The initial *cis*-**3** has three bands in its spectrum at 760, 755 and 729 cm^{-1}; after deuteration, only the bands at 760, 715 cm^{-1} are revealed. Hence, PIHE involves not only vinylic hydrogen (the principal direction), but also benzene hydrogens.

From these results, the following conclusions can be made:

(i) *cis*-Ethylenes, as more thermodynamically unstable compounds, are involved in PIHE to a greater extent than their *trans* isomers.

(ii) PIHE can be followed by *cis*/*trans* isomerization (but not by *trans*/*cis* isomerization).

(iii) Homoaromatic ethylene **1** enters into PIHE at the α position [3]. The cause of such behaviour is quite clear: α-stabilized carboanion is produced before formation of the C–D bond.

(iv) Ferrocenyl ethylene **2** enters into PIHE at mainly the 3 and 5 positions. This feature is a result of the push-pull interaction between the ferrocenyl and nitro groups; the acidity of α-ethylenic protons is decreased, but the acidity of the aromatic *ortho* protons (which are activated by the nitro group) remains sufficient for the reaction of H^+/D^+ exchange, although its depth is depressed.

(v) The location of the nitro group in the *ortho* position in respect of the ethylenic fragment in *cis*-**3** leads to activation of the α-ethylenic proton with revival of its acidity. This effect is observed exclusively for the *cis* isomer of **3**; *trans*-**3** is stubborn against PIHE. Steric conditions in the *cis* isomer are probably more favourable than in the *trans* isomer with respect to the formation of the intramolecular bond ONO $\cdot\cdots\cdot$ HC. Such hydrogen bonds results in electron shift from the α-CH bond to the NO_2 group, and that assists in α-CH participation in PIHE. In general, *cis* isomers are considered to be more active in PIHE than *trans* isomers.

(vi) The absence of the nitro group abolishes the PIHE ability of *cis* and *trans* ferrocenylethylenes **5**.

(vii) Ferrocenyl ethylenes **4**, with a *meta*-nitrophenyl fragment, do not take part in PIHE (refers to *cis* and *trans* isomers). The conjugation between the nitro group and the ferrocenyl fragment is a condition of PIHE proceeding.

(viii) The analogues **6** and **7**, which do not contain the ferrocenyl ethylenic moiety, do not enter into PIHE.

Ferrocenyl(nitrophenyl)ethylenes **2** behave in a special manner in PIHE.

References

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