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Behaviour of β -ferrocenylacrylonitrile in reactions with organic bases

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Abstract

β -Ferrocenylacrylonitrile forms nitrile-stabilized α -carboanion under the action of alkoxy-anions, and yields the anion-radical in the reaction with cyclooctatetraene dianion but undergoes no changes in the presence of aromatic and aliphatic amines. The α -carboanion retains the geometry of the original β -ferrocenylacrylonitrile, whereas the anion-radical undergoes *cis/trans*- (rather than *trans/cis*)-isomerization.

Introduction

β -Ferrocenylacrylonitrile (**1**) contains an ethylenic bond which is simultaneously affected by the acceptor (CN) and donor (Fc) substituents. Here the interactions of this compound with organic bases of various classes are described.

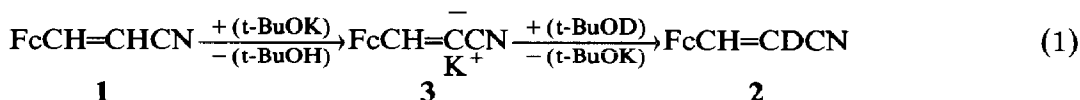
Interaction with amines

Some of the interactions of substrate **1** with amines: aliphatic (*N,N,N',N'*-tetramethylethylenediamine), heterocyclic (morpholine) and aromatic (tris(*p-N,N*-dimethylaminophenyl)carbinol) have been examined. No changes in the substrate are observed in either of these cases, and is irrespective of whether the substrate used was in the *cis*- or the *trans*-form. The substrate reversions are quantitative.

Interaction with alcoholates

The reaction of **1** with potassium ethylate and *t*-butylate has been studied. The relevant alcohol, deuterated at the hydroxy group was used as medium. The reaction was performed in this alcohol only, or in a mixture of equal volumes of the alcohol and THF. It was found that in the presence of *t*-BuOK or EtOK *cis*- or *trans*-**1** react

with *t*-BuOD or EtOD by isotopic exchange of hydrogen (at 50 °C). α -Deuterio-derivatives (**2**) are formed in this case. The label occupies the geminal position in respect of the nitrile group, the geometry of the original ethylene remains practically constant; the yields are almost 90%, the content of deuterium in the *cis*- and *trans*-**2** obtained $\leq 95\%$. The H–D exchange affects only one of the CH groups irrespective of the basicity of the medium (1 *M* or 2 *M* relative to the alcoholate) or the concentration of the deuterium donor (the alcohol-THF mixture (1:1) or pure alcohol). The transformation is depicted in eq. 1.



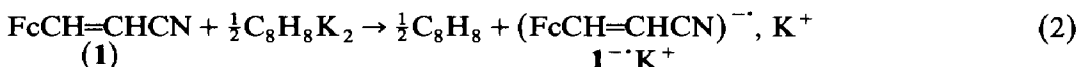
The reaction scheme takes into account the stabilization of the carboanion centre in salt **3** by the neighbouring cyano group. If this scheme is valid, then it unexpectedly follows that anion (FcCH=CCN)[−] is incapable of isomerization.

It has been found [1] that in the presence of *t*-BuOK in *t*-BuOD-THF (1:1) solution, *cis*-4-nitrostilbene (**4**) forms a mixture of *cis*- and *trans*-isomers (at 50 °C) and the H–D exchange takes place at the α -position of the ethylenic bond.

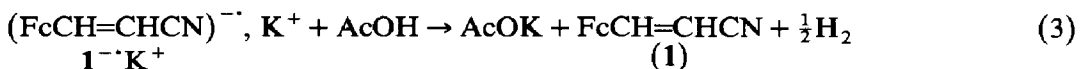
The CN group is a less strong acceptor than NO₂, whereas the Fc group is a much stronger donor than Ph. **1** must therefore show less affinity for the electron than molecule **4**. If this is the case then *t*-BuO[−] ion acts only as a proton acceptor towards **1** but towards substrate **4** it also acts as an electron donor, which is favourable for *cis/trans*-isomerization [2]. It is reasonable to assume that the carboanion formed from *cis*-**1** transforms into the *trans*-isomer more slowly than its removal of deuterium from *t*-BuOD. The resulting ethylene exhibits insufficient electron affinity to alkoxy anion, does not participate with the alkoxy ion in the electron transfer, and retains its geometry.

Interaction with cyclooctatetraene dianion

The reactions were carried out at −50 °C using the dipotassium salt of the cyclooctatetraene dianion (C₈H₈K₂) in THF solution. The transformations observed proceed according to eq. 2.

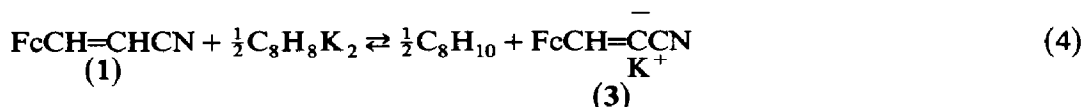


The cyclooctatetraene (C₈H₈) formed was identified by use of a GLC technique [3]; the anion radical salt $\mathbf{1}^{\cdot-}\text{K}^+$ produces a singlet in the ESR spectrum (−196 °C). Treatment of the mixture with 25% AcOH enables the isolation of neutral β -ferrocenylacrylonitrile in almost quantitative yield (eq. 3).



If substrate **1** is introduced into the reaction as the *trans*-isomer, the entire reversed product acquires the *trans*-configuration. Under these conditions, *cis*-**1** yields a mixture consisting of a *trans*- (70%) and the original *cis*-isomers (25%). The test experiment has shown that the treatment of *cis*-**1** with 25% AcOH in THF does not produce the *trans*-isomer.

$C_8H_8K_2$ can act both as electron donor and as proton acceptor towards ferrocenylethylene. The anion-radical (cf. ref. 2) and carboanion mechanisms are possible for the *cis/trans* conversion mentioned here. The carboanion mechanism can be realized under the conditions of reactions (2) and (3) despite the fact that under the conditions of reaction 1 the corresponding carboanion added deuterium more rapidly than it underwent isomerization. The formation of carboanion is quite probable if one takes into account that β -ferrocenylacrylonitrile is CH-acid and $C_8H_8K_2$ is the base (eq. 4).



If the process proceeds according to mechanism 4, then, upon addition of heavy water, the H-D exchange could be confirmed from eq. 5.



The mass spectrum of the sample obtained in the conditions of reaction 5 has shown that deuteration does not occur. It is clear, however, that the inability of $C_8H_8K_2$ to detach proton from β -ferrocenylacrylonitrile should not be based exclusively on the absence of the deuterium label in the samples obtained after the decomposition of mixtures by deuterated water. If the H-D exchange in 1 proceeds slowly, then the stationary concentration of carboanion (3) will be very small. In this case, after addition of D_2O , the amount of the deuterio product 2 will also be very small. Consequently, we thought that the studies should be supplemented with experiments in which the deuterated reagent was constantly present in the reaction domain. To this end, we introduced β -ferrocenyl- α -deuterioacrylonitrile into reaction 4, that with $C_8H_8K_2$.

It is evident that this reaction forms an equilibrium and should result in a gradual washing out of deuterium from 2 with accumulation of the undeuterated ethylene 1. The geometric isomers of ferrocenylacrylonitrile produced by reaction 4 contained approximately the same amount of deuterium as the original samples. This result indicates that when deuterated β -ferrocenylacrylonitrile reacts with $C_8H_8K_2$, no noticeable detachment of deuterium, as in reaction scheme 4, takes place and only the electron transfer as outlined in scheme 2 occurs. Since free rotation around the ethylenic bond is prevented, we suggest that the isomerization of compounds 1 and 2 is due exclusively to electron transfer. At the same time it is noteworthy that the aromatic derivatives of acrylonitrile dimerize on entering into the electron transfer. The presence of the ferrocenyl substituent in the acrylonitrile molecule adds to the stability of the anion-radicals and prevents their dimerization.

Comparison of the behaviour of the *cis*-isomers of 1 with those of 2 under the conditions of reactions 2 and 3 revealed that the H-D isotopic substitution at the ethylenic bond has influence on the ability of the compound to isomerize upon one-electron transfer. In strictly correlated conditions both substrates 1 and 2 are changed into a mixture of the *cis*- and *trans*-isomers (the total yield is more than 90%). In this case 2 containing only one deuterium atom, isomerizes less readily than the related H analog: the degree of conversion is 50 and 70%, respectively. Upon electron transfer the degree of *cis/trans*-conversion is changed noticeably even when the fragments in motion contain only a single atom of D.

Conclusion

A new approach to the investigation of the reaction mechanism of organometallic compounds by means of introducing an ethylenic bond into their molecules is suggested. The non-coordinated ethylenic bond acts as the inner stereo-indicator fragment. If the reagent does not add to this bond, the conformation stability of the latter indicates the absence of a donor-acceptor interaction*. This may be exemplified by the interaction between β -ferrocenylacrylonitrile and amines. If ethylene-containing organometallic compounds enter into acid-base interaction to yield the carboanion centre at the ethylenic bond, then in terms of the geometry of the products resulting from the carboanion protonation, we can suggest reasons for the conformational stability of this carboanion. The interaction β -ferrocenylacrylonitrile with alcoholates for example has confirmed that the resulting carboanion participates in the H-D exchange without undergoing any noticeable isomerization. If ethylene-containing organometallic compounds enter into the electron transfer to yield anion-radicals, then the *cis/trans* conversion of the ethylenic fragments would indicate this process. The approach described above is also useful for discerning the finer (delicate) isotopic effects: the substitution of only one H atom at the ethylenic bond of β -ferrocenylacrylonitrile for D results in a decreased conversion of the indicator fragment by a factor of ~ 1.5 .

Experimental

The NMR spectra were recorded by means of a Bruker WP-200 instrument at the working frequency of 200 MHz, in CCl_4 solutions and with TMS as a reference. The mass spectra were obtained by means of AEI MS-30 instrument equipped with an automatic data collecting system (DS-50), the ionization voltage was 70 eV. The deuterium content in the samples obtained was determined from the intensity of the peaks of the molecular ion (M^+) as well as those of the $(M - \text{Cp})^-$ fragment ion in the mass spectra using the "ISOMETA" program for calculations [5]. The ESR signals were recorded on a RE-1301 instrument.

A procedure described previously [6], was used to make β -ferrocenylacrylonitrile **1** as the *cis*- and *trans*-isomer mixture; the isomers were separated by TLC on L 40/100 silica gel with hexane-benzene (1:3) as eluent. The various bands of the isomers were separated mechanically. Extraction of the fractions was performed with ether and work-up gave *cis*-**1**, m.p. 82–84°C, and *trans*-**1**, m.p. 92–93°C. The samples also gave differing PMR spectra (δ): *cis*-**1** 4.24 and 4.41, 4H, C_5H_4 , 4.74, 5H, C_5H_5 , 5.21d, 1H, CH, 6.88d, 1H, CH $^3J(\text{H}^1-\text{H}^2)$ 10 Hz; *trans*-**1** 4.21 and 4.37, 4H, C_5H_4 , 4.71, 5H, C_5H_5 , 5.37d, 1H, CH, 7.24d, 1H, CH $^3J(\text{H}^1-\text{H}^2)$ 15 Hz.

The signals from the ethylenic protons were identified on the basis of the Pascal et al. equation [7] which links the chemical shifts of these protons with the Z-parameters of the ethylenic proton shielding:

$$\delta(\text{C}=\text{C}-\text{H}) = 5.25 + Z_{gem} + Z_{cis} + Z_{trans}$$

* Upon bonding the ethylenic compounds can also isomerize into charge transfer complexes [4].

The effect of the ferrocenyl substituent was expressed in terms of the relative parameters of the aryl group, see Table VI.10 in ref. 7.

The low field shifts were found to correspond to the protons in the β position of the ethylenic bond, and those at high field were found to correspond to protons in the α position.

Interaction of cis- β -ferrocenylacrylonitrile (1) with amines (exemplified by morpholine)

A mixture of 3 mmole of cis-1 and 6 mmole of morpholine was stirred, in 10 ml of a THF-absolute alcohol mixture (1 : 1) or without solvent, at 25°C for 24 hours. No colour changes occurred nor were paramagnetic particles formed (monitoring with ESR). The product was separated by TLC on L 40/100 silica gel, hexane-benzene (1 : 3) was used as eluent. The single band eluted was, separated and extracted with ether. The cis-1 was isolated in 95–98% yield; a sample of cis-1 obtained mixed with an authentic sample showed no depression of the melting point.

Isotopic exchange of hydrogen in cis- and trans-1

1 (0.6 mmole) was stirred with 5 ml of the t-BuOD-THF mixture or 5 ml of pure t-BuOD or EtOD, in which some metallic potassium (0.04 mg-atom) had been dissolved, in the absence of oxygen and moisture at 50°C during 4 hours. The mixture was then stored for 12 hours at 25°C, the solvent was removed in vacuum, and the residue was extracted with absolute ether. The extract was filtered off, evaporated and chromatographed on a thin layer of silica gel in the conditions described above. The chromatograms indicated the formation of isomerization products in trace, non-extractable, amounts. Up to 0.55 mmole of cis- and trans-isomeric products of the H–D exchange were obtained from various runs, along with yields of up to 90% and deuterium contents of 95 and 85%, respectively for the initial cis and trans substrates. The H–D exchange correlates with a complete or practically complete disappearance of the high field signal of the ethylenic protons in the PMR spectra of the samples obtained from cis- and trans-1 after the isotopic exchange. In this case, the relative intensity of all the other signals remains the same. The resulting substances were identified as cis- and trans- β -ferrocenyl- α -deuterio-acrylonitrile, m.p. 84.5 and 93.5°C, respectively.

Interaction of cis- and trans- β -ferrocenylacrylonitriles (1) and their 2-deuterio analogs (2) with cyclooctatetraendipotassium ($C_8H_8K_2$)

The reagents were stirred in THF (argon) (1 mmole of substrate 1 or 2 was taken per 0.5 mmole of $C_8H_8K_2$) and stored at –40°C for 30 min. The solution was cooled to –100°C and the singlet ESR signals were recorded; any rise temperature resulted in signal disappearance. When the stirring was over, 1 ml of 25% AcOH at –5°C was added and the solution was immediately treated to give separately the cis- and trans products by TLC in the conditions described above. 0.9 mmole of cis- and trans-1 or -2 were obtained. The ratio of trans : cis was found to be to 2.25 for 1 and 0.975 for substrate 2. The deuterium content in the samples obtained is practically the same as that of the original (as determined from PMR spectral data and by mass spectrometry).

References

- 1 D.H. Hunter and D.J. Gram, *J. Am. Chem. Soc.*, 88 (1966) 5765.
- 2 Z.V. Todres, *Uspekhi Khimii*, 43 (1974) 2274.

- 3 Z.V. Todres, Yu.I. Lyakhovetskii and D.N. Kursanov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1969) 1415.
- 4 Z.V. Todres, T.T. Kuryaeva, H.L. Ryzhova and D.N. Kursanov, *Dokl. Akad. Nauk SSSR*, 240 (1978) 1372.
- 5 Yu.N. Sukharev and Yu.S. Nekrasov, *Org. Mass Spectrom.*, 11 (1976) 1239.
- 6 T.P. Vishnyakova and A.A. Koridze, *J. Obshch. Khimii*, 39 (1969) 210.
- 7 B.I. Ionin, B.A. Ershov and A.I. Kol'tsov, *NMR Spectroscopy in Organic Chemistry (In Russian)*, Khimia Publishers, Leningrad, 1983, p. 157.