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Cis / trans isomerization of β-ferrocenylacrylonitrile during protophylic isotope hydrogen exchange

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Abstract

The behaviour of β-ferrocenylacrylonitrile in the presence of ^{t}BuOK in a mixture of THF with ^{t}BuOD and in pure THF are compared. Carbanion formation is shown to be a result of proton abstraction from the ethylenic bond at the geminal position onto the nitrile group. In the presence of alcohol, the carbanion is deuterized (protonized) without visible *cis / trans* isomerization. In the absence of alcohol, *cis / trans* conversion does take place. The conclusion has been drawn that the isomerization rate is much lower than the deuteration (protonation) rate.

Hunter and Cram [1,2] studied the kinetics of base-catalysed isomerization and isotope H/D exchange of *cis* and *trans* stilbenes and their methyl derivatives. The authors suggested that both reactions proceeded through an allylic or vinylic anion as an intermediate. *Cis / trans* isomerization and H/D exchange rates depend on the nature of stilbene and on the composition of the reaction mixture (^{t}BuOK in ^{t}BuOD or in ^{t}BuOD + THF or in ^{t}BuOD + DMSO). Both reactions are accelerated, but to a different extent, by the introduction of an electron acceptor substituent in the benzene ring as well as increased basicity of the medium.

Similar reactions with the compounds containing an organometallic fragment at the ethylenic bond have been studied. Recently, we investigated H/D exchange of β-ferrocenylacrylonitrile (**I**) in the presence of ^{t}BuOK in ^{t}BuOD and THF [3]. It was established that deuteration takes place, the label occupies the *geminal* position in respect of the nitrile group, and the geometry of the original ethylene remains practically constant. The formation of the anion $FcCH{=}\bar{C}CN$ was suggested as the first step of the H/D exchange reaction; this anion adds ion D^+ promptly, *cis / trans* isomerization proceeds at a limited rate (or does not proceed at all) [3].

In the present work, we studied the interaction between *cis*-**I** and ^{t}BuOK in THF without any alcohol (which was used previously as a donor of D^+). In other

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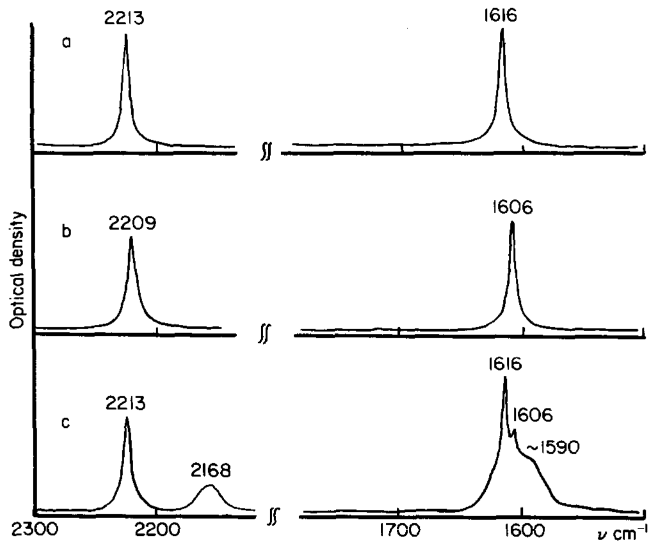

Fig. 1. Infrared spectra of the β-ferrocenylacrylonitrile solutions in THF: (a) *trans* isomer; (b) *cis* isomer; (c) *cis* isomer with ᵗBuOK.

respects, the reaction conditions were the same as for the H/D exchange reaction. The reaction was controlled by Fourier transform IR spectroscopy (see Experimental). The spectra are reproduced in Fig. 1a–c. The spectra show that *cis*-I forms vinylic anion (II) according to the hydrogen abstraction reaction:

$$\underset{\text{(I)}}{\text{FcCH=CHCN}} + {}^{t}\text{BuOK} \overset{\text{THF}}{\rightleftharpoons} \underset{\text{(II)}}{\text{FcCH=}\bar{\text{C}}\text{CN}(\text{K}^{+})} + {}^{t}\text{BuOH}$$

The reaction is reversible, so the resulting vinylic anion can be protonated by ᵗBuOH, which is the second product of the hydrogen abstraction process. As can be seen from the reaction equation, the inclination of the anion **II** to *cis/trans* isomerization appears by the bands belonging to either *trans*-**II** or *trans*-**I**.

The spectrum (Fig. 1c) contains broad bands at 2168 cm^{-1} with $\Delta\nu_{1/2} = 30$ cm^{-1} and *ca.* 1590 cm^{-1} with $\Delta\nu_{1/2} = 60$ cm^{-1}, which can be assigned to the stretching vibrations of the nitrile and the ethylenic bonds of the nitrile-stabilized anion **II**. But it is impossible to distinguish whether it is a *cis* or *trans* isomer. ᵗBuOH formation is revealed by a broad weak band ν(OH) with maximum at 3490 cm^{-1}. In contrast to carbanion **II**, the *cis* and *trans* isomers of the ethylene **I** are easily recognized by their absorbance in the region 2300–1500 cm^{-1}. As is seen from Fig. 1a,b, the spectrum of the *cis* isomer contains intensive bands ν(C≡N) and ν(C=C) at at 2209 and 1606 cm^{-1}, respectively, and *trans* isomer at 2213 and 1616 cm^{-1}. In the spectrum of *cis*-I with equimolar amounts of ᵗBuOK (Fig. 1c), bands for both isomers were observed. On the basis of the relative intensity of the bands, it may be concluded that the amount of *trans* isomer is greater than that of *cis* isomer.

Thus, it has been shown by IR spectroscopy that *cis*-I forms the vinylic anion **II** as a result of action of ᵗBuOK in THF solution. The anion does incline to *cis/trans* isomerization. The positions of the anion bands together with their integral intensity reflect the high degree of conjugation in the anion **II**. For this reason, the negative charge is partly delocalized, resulting in definite stability of the anion **II**. The latter has not only thermodynamic but also geometric stability. Probably, it is due to the relative geometric stability of the anion, that the H/D exchange rate is far higher than the rate of *cis*/*trans* isomerization. In accordance with that, the isomerization did not take place to any appreciable extent during the protophylic H/D exchange of *cis*-**I** [3].

Under the same conditions, the behaviour of *cis*-stilbene was found to be similiar [1]. Kinetic measurements have shown that the H/D exchange rate in the presence of ^{t}BuOK exceeds the isomerization rate by a factor of 2500. That is why the H/D exchange proceeds via the retention of the *cis*-stilbene configuration; the yield of deuterated *trans* isomer is no more than 1% [1]. The introduction of the electron accepting nitro group into one of the benzene rings of *cis*-stilbene lowers the ratio of the rate constants of the isotope exchange reaction and isomerization, to close to unity. For *cis*-4-nitrostilbene, the H/D exchange reaction leads to 48% of deuterated *cis* isomer and 49% of *trans* isomer [1]. Ethylene **I** contains either donor (Fc) or acceptor (CN) substituents, thus their mutual influence is compensated. It stands to reason, that ethylene **I** behaves similar to *cis*-stilbene in the H/D exchange reaction.

Experimental

Freshly prepared dry ^{t}BuOK (0.6 mmol) was stirred with *cis*-β-ferrocenylacrylonitrile (0.6 mmol) in 5 ml of absolute THF for 4 h at 50°C. The mixture was then exposed for 12 h at 25°C and the IR spectrum was recorded. All operations were carried out under dry argon. The IR spectra were recorded with an infrared Fourier transform spectrometer (Bruker IFS-25) with a resolution of 2 cm^{-1}. The solvent absorption was subtracted. A KBr cell (0.12 mm thick) was used. The chemical experiments and the spectral measurements were repeated many times. The spectral data reproduced well. Increase of the exposure period to 6 h and longer, did not result in significant changes. A control experiment was also performed: *cis*-I was heated in THF at 50°C for 4 h in the absence of ^{t}BuOK; the IR spectrum was then recorded.

In the spectrum, only the bands of the initial *cis*-I were recorded. To check for the presence of a paramagnetic particle, a probe was inserted into the reaction mixture in an ampoule and was examined by means of a Varian E12A EPR instrument. No EPR signal was found.

References

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