cis-trans ISOMERIZATION OF NITROSTILBENES IN THE PRESENCE OF AROMATIC AMINES

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Previously we had established that stilbenes, which contain a nitro group in either the aromatic ring or at the double bond, undergo cis-trans isomerization in the presence of aromatic amines [1]. The reasons for this phenomenon are discussed in the present paper. The possible mechanisms of the isomerization should be examined.

1. Formation of the charge-transfer complex (CTC).

cis-(I)

2. Cleavage of a proton at the ethylene bond of the base and subsequent addition of this proton to the isomerized fragment.

$$\operatorname{cis-}(I) + \operatorname{H}_{2}\operatorname{NAr}' \to \begin{bmatrix} H \\ Ar - \overline{C} = C - Ar \\ H_{3} \overset{\dagger}{\operatorname{N}} Ar' \end{bmatrix} \to \operatorname{trans-}(I) + \operatorname{H}_{2}\operatorname{NAr}'$$
(2)

3. Addition of the amine to the double bond and its subsequent cleavage from the isomerized fragment as the bipolar ion.

$$\operatorname{cis-}(I) + \operatorname{H_2NAr'} \to \begin{bmatrix} H & H \\ | & | \\ \operatorname{Ar-C-C-C-Ar} \\ | & | \\ \operatorname{H_2NAr'} \\ + \end{bmatrix} \to \begin{bmatrix} H \\ \operatorname{Ar-C-C-C-Ar} \\ | & | \\ \operatorname{H_2NAr'} \\ H \end{bmatrix} \to \operatorname{trans-}(I) + \operatorname{H_2NAr'}$$
(3)

4. Formation of ion-radicals as the result of reversible electron transfer.

$$\operatorname{cis}(\mathbf{I}) + \operatorname{H}_{2}\operatorname{NAr}' \rightarrow \begin{bmatrix} \mathbf{H} & \mathbf{H} \\ \mathbf{I} & \mathbf{I} \\ \operatorname{Ar}-\mathbf{C} = \mathbf{C} - \operatorname{Ar} \end{bmatrix}^{+} + \operatorname{H}_{2}\operatorname{NAr}' \rightarrow \begin{bmatrix} \mathbf{H} \\ \mathbf{I} \\ \operatorname{Ar}-\mathbf{C} = \mathbf{C} - \operatorname{Ar} \\ \mathbf{I} \\ \mathbf{H} \end{bmatrix}^{+} + \operatorname{H}_{2}\operatorname{NAr}' \rightarrow \operatorname{trans}(\mathbf{I}) + \operatorname{H}_{2}\operatorname{NAr}'$$

$$(4)$$

It should be mentioned that the formation of carbanions by Scheme (2), of bipolar ions by Scheme (3), or of ion radicals by Scheme (4) can include the initial step of forming the CTC.

Arguments that relate to each of these four mechanisms are discussed below. The nitrostilbenes, listed in Table 1, gave colored solutions in the presence of aromatic amines like aniline, p-toluidine, N,N-dimethylaniline, and N,N-tetramethyl-p-phenylenediamine, in which connection, based on the EPR data, paramagnetic particles are not formed here. All of the studied compounds, except cis-2,4-dinitrostilbene (DNS), slowly changed from the cis to the trans form under the influence of the amines; characteristic examples are indicated in Table 2. Dilution of the stilbene-amine mixtures with an inert solvent to concentrations that are convenient for recording the electronic spectra led to decomposition of the complexes to the starting components. An exception were the α,β -DNS and 2,4-DNS, whose complexes with aromatic amines are also retained on dilution, which made it possible to establish the presence of the charge-transfer band, which shifts toward longer wavelengths with increase in the donor capacity of the amine. Thus, in the presence of aniline the cis- and trans- α,β -DNS display the charge-transfer band at 365 nm, and at 385 nm in the

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1602-1605, July, 1980. Original article submitted June 26, 1979.

TABLE 1. Characteristics of Compounds Used

· · · · · · · · · · · · · · · · · · ·	mp, °C		
Compound	our data	literature data	
cis - α , β -Dinitrostilbene trans - α , β -Dinitrostilbene trans -4-Nitrostilbene cis -4-Nitrostilbene cis - α -Nitrostilbene cis - α -Nitrostilbene trans -4,4' -Dinitrostilbene cis -2,4-Dinitrostilbene trans -2, 4-Dinitrostilbene	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	109 [2] 186 [2] 158 [3] 58 [4] 74 [5] 188 [4] 280 [4] 127 [6] 140 [6]	

TABLE 2. Degree of Isomerization of Nitrostilbenes (donor:acceptor ratio = 1:1, kept at 25°C without direct light or in a dark chamber)

Stilbene	Amine	Holding time, h	Yield of trans isomer, %*
cis-α,β-Dinitrostilbene	Aniline	4	50
m .	N,N-Dimethyl- aniline	4	42
cis-α-Nitrostilbene	Aniline	4	16
cis-4-Nítrostilbene		10	6

*In all of the experiments the sum total of the recovered nitrostilbenes as the cis and trans forms was 80-90%.

presence of p-toluidine; here the solvent was hexane. In the presence of aniline the cisand trans-2,4-DNS display in hexane the charge-transfer band at 360 nm, and at 370 nm in the presence of N,N-dimethylaniline. Using the method given in [7], it was found from the UV spectra that the formed complexes have a 1:1 composition, while the stability constants, determined by the method given in [8], are equal to 0.3-0.4 liter/mole. Consequently, the initial step in the reaction of the discussed nitrostilbenes with amines is the formation of the CTC, even though the latter are comparatively weak complexes.

It is important that of the studied dinitro compounds only the 2,4-DNS, which is stable even with a 3-5-fold excess of the amine, fails to undergo cis-trans isomerization under the influence of amines, although, based on the data given in [6], the trans-2,4-DNS is more stable than the cis isomer. It is obvious that the presence of two nitro groups in one nucleus prevents isomerization, since the electron density, which shifts from the donor to the acceptor, is localized entirely within the limits of this nucleus. In this case the isomerization of the cis-2,4-DNS should also not be observed during the transfer of a single charge. Actually, either the one- or two-electron reduction by the cyclooctatetraene dianion (COT DA) in THF fails to change the configuration of the cis-2,4-DNS. As was shown by the check experiments, the trans-2,4-DNS also does not change to the cis form under these conditions. At the same time, a spacing of the nitro groups along two different nuclei facilitates cis-trans isomerization during the transfer of either one or two electrons: the cis-4,4'-DNS under the influence of the COT DA changes completely to the trans form, whereas the trans-4.4'-DNS is not isomerized under these conditions [9]. In the case of the amine cleaving a proton from the double bond by Scheme (2) or by the formation of the bipolar ion [Scheme (3)] the cis-2,4-DNS should undergo isomerization on a par with all of the remaining acceptors.

If a mixture of cis- α -nitrostilbene and aniline is kept for 4 h at 25°, followed by treatment with a 15% solution of DCl in D₂O, then a mixture of the cis and trans isomers of the starting compound separates, in which isomers the C-D bonds are absent, which was established by analysis of the combustion water and by mass spectrometry. Consequently, the cleavage by aniline of a vinyl proton by Scheme (2) cannot be regarded as a reason for cis-trans isomerization.

From Table 2 it can be seen that for the reaction of $cis-\alpha,\beta$ -DNS with aniline the halfreaction time is 4 h. In N,N-dimethylaniline the amino group is shielded, and its addition to the nitrostilbene by Scheme (3) is difficult. However, in the presence of dimethylaniline the α,β -DNS undergoes isomerization with approximately the same half-reaction time.

We also studied the reaction of 4-nitrostilbene and the DNS, listed in Table 1, with the aliphatic amines: di- and triethylamine and tributylamine, which, when compared with aniline and its derivatives, have a much greater basicity but a smaller polarizability. It was established that in the presence of aliphatic amines neither the formation of the CTC nor the cis-trans isomerization of the stilbenes is observed.

The presented results show that the cleavage of H from the ethylene bond of the nitrostilbene by the amine or the addition of the amine to this bond cannot be regarded as reasons for the isomerization.

Reversible electron transfer is very difficult to observe if it is very fast: a broadening of the signal occurs in the EPR spectrum, which can prevent its detection. It should be mentioned that the studied nitrostilbenes isomerize rapidly during electron transfer [9]. In the presence of aromatic amines the cis-trans isomerization of the same nitrostilbenes goes slowly, in which connection the relative rate correlates with the degree of stability of the corresponding CTC. As can be seen from Table 2, several tens of hours are required for isomerization when the complexes are less stable, or up to ten hours when the complexes have a greater stability. The cis- α -nitrostilbene represents a special case, the isomerization of which is detected only in the presence of an aromatic amine. During electron transfer this acceptor gives an exceedingly reactive radical, which dimerizes immediately after formation.* As a result, in the reaction with aromatic amines the cis- α -nitro-

 $\begin{array}{c} H & NO_{2} \\ \downarrow & \downarrow \\ Ph-C=C-Ph \end{array} \xrightarrow{+e} \left[\begin{array}{c} H & NO_{2} \\ \downarrow & \downarrow \\ Ph-C=C-Ph \end{array} \right] \xrightarrow{-} H & NOO^{-} \\ \downarrow & \parallel \\ H & Ph-C-C-Ph \xrightarrow{+} \frac{1}{2} \xrightarrow{-} OON = C(Ph)CH(Ph)CH(Ph)C(Ph) = NOO^{-} \end{array}$

stilbene functions as a peculiar stereo indicator, which indicates the absence of electron transfer.

The formation of the CTC, which causes the ethylene bond to be enriched with excess electron density, can be regarded to be the sole remaining reason for the isomerization. A decrease in the order of magnitude of the α,β bond should occur as a result of this, since the excess charge migrates to lower vacant orbitals, which in the nitrostilbenes (based on the data given in [10]) are antibonding in the vicinity of the $C_{\alpha}=C_{\beta}$ bond. This facilitates a change in the configuration of the olefinic bond in the CTC: the excess electron density migrates from the higher occupied orbital of the donor to the lower vacant orbital of the acceptor.

EXPERIMENTAL

The preparation procedure and the characteristics of the employed nitro derivatives of stilbene are given in Table 1.

Isomerization of Nitrostilbenes in Presence of Amines. One mmole of the appropriate nitro- or dinitrostilbene was dissolved in 1-3 mmoles of aniline or dimethylaniline. The mixture was kept for the given length of time and then was separated by TLC. In some experiments the mixture prior to separation was diluted with organic solvents (hexane, methanol, acetonitrile, THF). At times the amine was removed by treatment with 15% aqueous HCl solution. A 15% solution of DCl in D₂O was used in individual experiments, in which connection the control experiments disclosed that the starting nitrostilbenes are not isomerized by either HCl or DCl in D₂O. The obtained mixture as the eluent. The Al₂O₃ support alone does not cause the cis-trans isomerization of the studied compounds. In all cases the cis isomer is characterized by a higher R_f value, with the exception of the α,β -DNS, whose cis isomer is eluted with greater difficulty than the trans isomer. The Al₂O₃ fractions, containing either the cis or trans isomers, were eluted with acetone and then the solvent was distilled off. The isomers were identified by comparing the melting points and IR spectra of the obtained compounds and the standards.

*Shown in a joint paper with T. M. Chernyshova.

<u>One-Electron Reduction of 2,4-Dinitrostilbene</u>. A solution of 0.013 mmole of either the cis- or trans-2,4-DNS in 1.5 ml of THF was mixed with a solution of 0.013 mmole of the dipotassium salt of the COT DA in 30 ml of THF [9] at -40° under argon. The solution turned red.* The mixture was kept for 30 min at -40°, and then the temperature was raised to -5° and 1 ml of 25% AcOH solution, free of air, was added. The solution became clear. It was evaporated in vacuo and the residue was separated on Al₂O₃, using a 1:2 hexane-benzene mixture as the eluent. The COT remained at the start, while the starting 2,4-DNS isomer, after extraction of the corresponding band with acetone, was recovered in up to 95% yield (the mixed melting point with an authentic sample was not depressed).

<u>Two-Electron Reduction of cis-2,4-Dinitrostilbene</u>. To 0.036 mmole of the cis-2,4-DNS in 2 ml of THF was added at -40° a solution of 0.019 mmole of the dipotassium salt of the COT DA. The solution turned dark red. After stirring for 15 min the temperature was raised to -5° and the mixture was worked up as described above. The starting cis-2,4-DNS was isolated in 92% yield, mp 126-127°.

CONCLUSIONS

The possible mechanisms for the cis-trans isomerization of nitrostilbenes in the presence of aromatic amines were discussed and it was shown that the reason for the isomerization is the formation of charge-transfer complexes.

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*A sample of the solution gives a singlet in the EPR spectrum.