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Cis/trans conversion of potassium derivatives of 2- and 4-nitrostilbenes

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Abstract

Potassium derivatives of 2- and 4-nitrostilbenes exist in non-dissociating solvents as coordination complexes with localization of the metal at the nitro group. Stilbene components of the complexes undergo *cis/trans* conversion, the extent of which does not exceed 50%. In conditions leading to disintegration of the complexes, the extent of conversion amounts to 100%.

Introduction

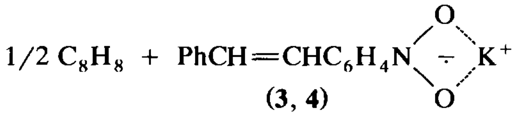
It has recently been revealed [1], that *cis* isomers of 2- and 4-nitrostilbenes (**1** and **2**) form 1 : 1 charge-transfer complexes with *N,N*-dimethylaniline and undergo *cis/trans* conversion. The isomerization was shown to proceed without abstraction of hydrogen from the CH=CH bond; it was not affected by impurities or oxygen and did not depend on the presence of paramagnetic particles (imineoxyl or cyclooctatetraene anion radical).

In the present paper, stereochemical transformations of prepared potassium derivatives of **1** and **2** are examined.

Coordination complexes between nitrostilbenes and potassium

The complexes were obtained by reaction of stilbenes **1** or **2** with cyclooctatetraene dipotassium ($C_8H_8K_2$):

$$\underset{(\mathbf{1},\,\mathbf{2})}{\mathrm{PhCH{=}CHC_6H_4NO_2}} + 1/2\ \mathrm{C_8H_8K_2} \xrightarrow{\mathrm{THF}}$$



$$1/2\ \mathrm{C_8H_8} + \underset{(\mathbf{3},\,\mathbf{4})}{\mathrm{PhCH{=}CHC_6H_4N}}\overset{\mathrm{O}}{\underset{\mathrm{O}}{\overset{\cdot\cdot}{\underset{\cdot\cdot}{\div}}}}\mathrm{K^+}$$

1, **3**: 4-NO_2; **2**, **4**: 2-NO_2

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The mixtures obtained were treated with oxygen or water or 25% acetic acid. In some of the runs, THF was partially removed; then the resulting suspensions were diluted with hexamethylphosphotriamide (HMPT) or a solid potassium precipitate (**3**, **4**) was filtered off. The potassium derivative of *cis*-**2** was much more soluble in THF than that of *cis*-**1**. Therefore, all experiments on solid samples were conducted with *cis*-**1**. The yield of dry complex **3** reached 97%, the yield of cyclooctatetraene (GLC determination in the reaction solution) was 100%.

Potassium derivative of *cis*-4-nitrostilbene (3)

This derivative gave a sharp singlet in the EPR spectrum; one potassium atom fitted one molecule of **1**; the sample contained up to 95% of paramagnetic component (determined by means of Faraday's method).

The initial compound *cis*-**1** had IR absorption bands ($\nu(NO_2)$) at 1350 and 1510 cm^{-1}; the potassium derivative **3** had bands ($\nu(NO_2^{-}K^{+})$) at 1375 and 1450 cm^{-1} (*cf*. ref. 2).

Complex **3**, dissolved in a mixture of dimethoxyethane with diethoxyethane, displayed an EPR spectrum containing a nitrogen triplet ($a_N = 8.9$ G), a proton doublet of the α-methine group ($a_H = 5.5$ G), and a triplet from protons of the nitrophenyl ring ($a_H^m = 1.25$ G, $a_H^o = 3.25$ G). There were no other lines. Within the phenomena of EPR, the delocalization of an unpaired electron has been revealed only for the fragment that includes the sequence of atoms $CHC_6H_4NO_2$. The EPR data show that, in ether solution, the potassium derivative **3** really exists as the coordination complex mentioned above. It is difficult for an unpaired electron to go out of the limit of the $CHC_6H_4NO_2$ fragment coordinated with the K^+ cation.

Complex **3** disintegrates in HMPT and the EPR spectrum is complicated, owing to the increasing degree of delocalization of an unpaired electron.

Dry solid potassium derivative **3** was treated with a specially prepared dried-out mixture of oxygen and nitrogen. As a result, complex **3** formed potassium superoxide and 4-nitrostilbene. The latter was recovered in 96% yield, consisting of 60%

Table 1

Interaction of *cis* isomers of 4- or 2-nitrostilbene (**1** or **2**) (1 mmol) with cyclooctatetraene dipotassium (0.5 mmol) (the results are averaged according to 3–5 experiments): solvent, THF; temperature, −40°C

No.	Stilbene	Treatment conditions			Isolated product	
		Solvent	Temperature (°C)	Addition (amount)	*trans* conversion (%)	Total yield (%)
1 [a]	1	Without	25	Without	40	96
2 [a]	1	THF	25	Without	40	94
3 [a]	1	HMPT	25	Without	100	93
4 [a]	1	THF	25	CE (1 mmol)	100	92
5	1	THF–HMPT (1:1)	−5	Without	100	94
6	1	THF	−5	Without	40	96
7	2	THF	−5	Without	30	98
8	2	THF	−5	CE (1 mmol)	100	98

[a] The experiments with preliminary isolated potassium derivative of **1** in the solid state.

initial *cis* isomer and 40% converted form (*trans* isomer) (see Table 1, run 1). In the form of a dry solid, transformation of the monopotassium derivative into the dipotassium derivative cannot proceed.

If the treatment of dry complex **3** is performed with oxygen in the medium of organic solvents, the results depend upon the nature of this solvent. In THF the same isomeric mixture is formed as in the case of the solid–gas reaction mentioned above. In HMPT and in THF in the presence of 18-crown-6-ether, the conversion degree reaches 100% (*cf*. runs 2–4, Table 1).

Complete isomerization was also achieved on conducting the reaction in a 1:1 mixture of THF and HMPT, without the isolation of dry complex **3** (Table 1, run 5). At the same time, conducting the reaction in pure THF, also without the isolation of **3**, resulted in 40% *cis/trans* conversion (Table 1, run 6).

Crown-ether, like HMPT, causes dissociation of coordination complex **3** with potassium. Naked 4-nitrostilbene anion-radicals are formed. Removal of potassium makes disproportionation of anion radicals difficult [3].

Treatment of complex **3** (before or after its disintegration) with 25% aqueous acetic acid or water, instead of oxygen, does not change the results. In a number of experiments, D_2O was used and H/D isotope exchange was not observed. In all cases, products of reduction of the nitro group were not found. Hence, potassium derivative **3** under the influence of protons or deuterons is subjected to one-electron oxidation, without any addition of H^+ or D^+ onto NO_2 or CH=CH groups. This result is unexpected so far as the potassium derivative of stilbene (without the nitro group) yields dibenzyl after protonation in THF [4]. In complex **3**, the extent of electronic saturation of the CH=CH fragment is enough for the isomerization, but not sufficient for proton (deuteron) addition.

The potassium derivative of *trans*-4-nitrostilbene, after the same treatment with oxygen or proton (deuteron) donors, yields neutral *trans*-4-nitrostilbene; *trans/cis* conversion does not take place.

Potassium derivative of *cis*-2-nitrostilbene 4

In potassium coordination complex **4** (with the $NO_2^{-}K^+$ fragment in the *ortho* position with respect to the CH=CH bond), significant steric hindrances can hamper *cis/trans* conversion. The logic of the study development required complex **4** to be probed also.

The latter was obtained by the reaction of *cis*-2-nitrostilbene (**2**) with $C_8H_8K_2$ (see above). In THF (Table 1, run 7), a complicated EPR spectrum was recorded although a nitrogen triplet, $a_N = 10.20$ G, was found. In the presence of crown-ether (see Table 1, run 8), the nitrogen triplet was characterized with a much smaller splitting constant, $a_N = 6.80$ G. This decrease in constant a_N undoubtedly testifies to the disintegration of complex **4**. Similarly, dissociation of the potassium–nitrobenzene coordination complex brings the constant a_N down, from 9.80 G to 8.48 G and the a_N of potassium 2-rhodanonitrobenzene decreases from 10.50 G to 5.50 G [5].

The solutions obtained, according to runs 7 and 8, were treated with 25% acetic acid and 2-nitrostilbene was quantitatively returned. In the presence of crown-ether, 2-nitrostilbene was obtained exclusively in *trans* form (Table 1, run 8) in spite of the fact that the pure *cis* isomer **2** was the substrate. In the absence of crown-ether

(Table 1, run 7), a mixture of *cis* and *trans* isomers was formed, with conversion degree equal to 30%.

Compared with the potassium derivative **3** under the same conditions (runs 1, 2, and 6, Table 1), one can conclude that the degree of *cis/trans* conversion of **4** (30% against 40%) is similar. Hence, steric hindrance of the *ortho* NO_2^{-} fragment is not essential for this kind of *cis/trans* conversion. *Trans/cis* Conversion is not observed in the case of 2-nitrostilbene either.

Conclusion

Forming monopotassium derivatives, *cis*-2- and *cis*-4-nitrostilbenes turn into the *trans* form. These forms occur as 30–40% admixtures in the case of stable complexes between nitrostilbenes and potassium. After disintegration of the complexes, only the converted form (*trans*) is found. The extent of the *cis/trans* conversion depends upon the safety of coordination complexes **3** or **4**. Such coordination prevents delocalization of an unpaired electron outside the limit of the nitrophenyl fragment and hampers rotation around the ethylenic bond.

In the same manner, a ball tied to a finger with a rubber lace flies on being struck until the rubber lace stretches out to its utmost, and then the ball sharply returns to the finger at the initial point of movement. Potassium acts similarly as a harpoon for moving electrons in complexes **3** and **4**.

Experimental

The following samples (crystallized from hexane) were used: *cis*-4-nitrostilbene, (**1**) m.p. 58–60°C, lit. 59–60°C [6]; *trans*-4-nitrostilbene, m.p. 156–158°C, lit. 157–158°C [7]; *cis*-2-nitrostilbene (**2**), m.p. 62–63°C, lit. 62.5–63.5°C [8]; *trans*-2-nitrostilbene, m.p. 70–71°C, lit. 70–71°C [8]. All the experiments were carried out under argon, and absolute solvents free from atmospheric oxygen were used.

Potassium derivatives of 1 and 2 (3 and 4, respectively)

Experiments without isolation of 3 or 4. A solution of 2 mmol of **1** or **2** in 25 ml of THF was mixed with a solution of 1 mmol of cyclooctatetraene dipotassium, $C_8H_8K_2$, in 30 ml of THF at −40°C. A dark-green suspension was formed; a probe exibited a sharp singlet in the EPR spectrum. The suspension was stirred for 30 min at −40°C, allowed to warm to −5°C and then 2 ml of 25% acetic acid, free from air, was added. In other experiments, the mixture was treated with dry oxygen. In both cases, the precipitate disappeared and the solution was decolorized. The yield of cyclooctatetraene, C_8H_8, was determined by GLC [9] and was found to be 100%. The reaction mixture was evaporated to two-thirds *in vacuo*, and separated with the help of TLC on Al_2O_3 (eluents hexane/benzene 4:5 or hexane/ether 3:4). At the start, C_8H_8 remained and the mixture of *cis* and *trans* isomers was divided into clear bands with R_f(*cis*) 0.80, R_f(*trans*) 0.55 in the case of 4-nitrostilbene and R_f(*cis*) 0.77, R_f(*trans*) 0.43 in the case of 2-nitrostilbene. The bands were separated mechanically and extracted with acetone. Removal of the solvent afforded 0.6–0.8 mmol of the *trans* isomer (30–40% of the mixture) and 1.3–1.1 mmol of the *cis* isomer (70–60% of the mixture). The total of nitrostilbenes returned was 90–95% of the initial amount. Mixing probes of the isolated substances with authentic samples did not decrease the melting points.

The control experiments with **1** or **2**, performed under the same conditions but without addition of $C_8H_8K_2$, did not lead to the isomerization of the initial *cis*-nitrostilbene (the sole spot in the TLC). For example, after removal of the solvent, **1** with m.p. 57–59°C was recovered quantitatively.

In a separate experiment, $C_8H_8K_2$ and **1** or **2** were mixed (proportions as mentioned above) using not pure THF but a 1:1 mixture with HMPT or THF containing 18-crown-6-ether (CE, 2 mmol). After stirring for 30 min at −40°C, dry oxygen was passed through the solution. TLC on Silufol UV-254 (eluent hexane/benzene 4:5) revealed only one spot of a *trans* isomer. The residue was washed with water after distillation of the solvent, *in vacuo*, and then crystallized from alcohol. From 2 mmol of **1** or **2**, 1.8 mmol of *trans*-4-nitrostilbene with m.p. 154–156°C was obtained; yield 90%. The mixing probe did not decrease the melting point.

Experiments with isolation of solid 3. A solution of **1** (2 mmol) in 25 ml of THF was mixed with a solution of $C_8H_8K_2$ (1 mmol) in 30 ml of THF at −40°C; the mixture was stirred for 30 min, 1 ml of probe was taken and mixed with 0.5 ml of 25% acetic acid. The analysis of the solution by GLC [9] showed that only C_8H_8 was contained in the reaction mixture and $C_8H_8K_2$ was spent completely. On overfreezing the solution *in vacuo*, a suspension was concentrated to one-third of the initial volume. Then the residue of **3** was filtered, suspended three times in hexane, then with pentane and dried *in vacuo*. Complex **3** (2.3 mmol) was obtained; yield 98%. Anal. Found %: C 63.43, H 4.35, K 15.50 (by residual ash). $C_{14}H_{11}NO_2K$ calc.: C 63.61, H 4.18, K 14.81%.

Simultaneously with the analyses, **3** (1.5 mmol) was treated with a dry mixture of oxygen and nitrogen for 1 h. The colour changed from dark-brown to yellow. The uncharged compound obtained was dissolved in 10 ml of THF. The solution was analyzed by means of Silufol TLC (see above). Two spots were revealed belonging to the *cis* and *trans* isomers of 4-nitrostilbene; the analysis was performed in the presence of witnesses. Then the mixture was preparatively divided using TLC (Al_2O_3, eluent hexane/ether 4:5). The isomers were isolated after the extraction of the divided bands with acetone. After solvent removal, 0.68 mmol of *cis* isomer and 0.46 mmol of *trans* isomer were obtained: total yield, 90%; converted form 40%. Mixing probes of isolated substances with authentic samples did not decrease the melting points.

During other experiments, **3** (0.9 mmol) was suspended in 20 ml of THF. After stirring for 30 min, the solution was treated with dry oxygen. As a result of a TLC probe of the solution on Silufol UV-254 (eluent hexane/benzene 4:5), the presence of two isomers was also established; they were divided in the same way as above: 0.26 mmol of *trans* isomer (40% from the mixture) and 0.39 mmol of *cis* isomer (60% from the mixture) were obtained. The total yield of nitrostilbene was 86%.

Further complex **3** (0.9 mmol) was dissolved in 20 ml of HMPT. After stirring for 30 min, the solution was treated with dry oxygen. Silufol TLC showed that only *trans*-4-nitrostilbene was present. HMPT was distilled *in vacuo* at 85–90°C, the residue was washed with water and crystallized from alcohol: 0.68 mmol of a substance with m.p. 156–157°C was obtained (yield 90%). Mixing a probe with an authentic sample of *trans*-4-nitrostilbene did not decrease the melting point.

As follows from control experiments, **1** is not isomerized in HMPT or in THF in the presence of CE.

Potassium derivatives of trans-4- or trans-2-nitrostilbene

A solution of 1 mmol of *trans*-nitrostilbene in 15 ml of THF was mixed with 0.5 mmol of $C_8H_8K_2$ at −40°C. A probe exhibited a sharp singlet in the EPR spectrum. After stirring for 30 min, the temperature was increased to −5°C and dry oxygen was passed through the reaction mixture (in other experiments 0.5 ml of 25% acetic acid was added). Disappearance of the precipitate and discolouration of the solution were observed. The GLC yield of C_8H_8 [9] was 100%. After partial evaporation of the solvent and TLC treatment of the residue (Al_2O_3), only *trans* isomers (without any isomerization) were isolated in yields up to 95%.

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