122. Electron-Transfer-Catalyzed *cis* → *trans* Isomerization of 1,1′-Azonorbornane[1])

Prototype of a Reversible Two-Stage Storage System

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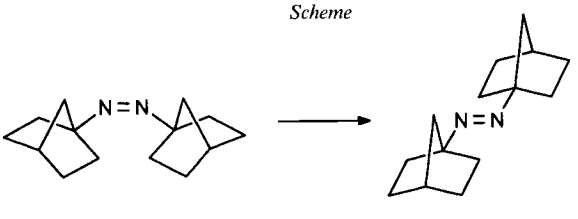
ESR and cyclic voltammetry investigations show that isomerization of the radical cation of *cis*-1,1′-azonorbornane (*cis*-**1**) to the *trans*-radical ion proceeds too fast in solution for direct investigation of the *cis*-radical ion even at −78°. The facile isomerization of the radical cation is in agreement with PM3 calculations proposing an activation barrier of only 17 kJ/mol. As a consequence, quantitative *cis* → *trans* isomerization of 1,1′-azonorbornane can effectively be accomplished by addition of catalytic amounts of one-electron oxidants. This is the first evidence for a radical-cation-catalyzed *cis* → *trans* isomerization of azo compounds.

Introduction. – Electron removal or electron addition are – apart from photochemical excitation – the simplest chemical transformations that can entirely change the structure, stability, and reactivity of a molecule [1]. At present, there is a lot of interest to understand the impact of electron transfer on ground-state molecules and to use the changed molecular properties for new reactions [2] [3]. Herein, we want to describe how electron removal can speed up the *cis* → *trans* isomerization of 1,1′-azonorbornane (**1**) by many orders of magnitude (*Scheme*).

Scheme



cis-**1** *trans*-**1**

We have been interested in the thermal *cis* → *trans* isomerization of aliphatic azo compounds for a long time [4]. Aside from *cis*-azobicyclo[2.1.1]hexane [5], *cis*-**1** (= (Z)-1,1′-azobicyclo[2.2.1]heptane) is one of the few acyclic *cis*-azoalkanes that can be handled

[1]) Electron-Transfer-Catalyzed Reactions, Part II. Part I: [2].

and purified at room temperature without isomerization [4] [6]. Thermal *cis* → *trans* isomerization of **1** proceeds at 91° with a half-life time of 1 h [7]. Many arguments support inversion at one N-atom as the most plausible mechanism for the thermal *cis* → *trans* isomerization [7] [8]. The driving force for the reaction is the high exothermicity of the isomerization ($\Delta H_{isom} = -68$ kJ/mol) [4] [7].

We have already been working on *cis*- and *trans*-azonorbornane radical-cation chemistry when a very recent paper by *Mendicino* and *Blackstock* [9] reported on the same system. Therein, *trans*-$\mathbf{1}^{+\cdot}$ was shown to be the first fluid-solution stable azoalkane radical cation, and the reported ESR and cyclic voltammetry data are in full agreement with our results [10]. The remarkable persistence of *trans*-$\mathbf{1}^{+\cdot}$ raised the question how electron removal would affect the *cis*-isomer and its isomerization.

Experimental. – Pure *cis*-**1** was prepared as described in [4]. For UV analysis, one chamber of a tandem cuvette was filled with 0.8 ml of a 0.018M *cis*-**1** soln. in MeCN and the other with 0.8 ml of the one-electron oxidant soln. in the same solvent. After mixing the *cis*-**1** and the oxidant solns., the UV/VIS absorption of *cis*-**1** was followed at 423 nm. Quant. analysis by GC with heptadecane as internal standard showed that > 99% of *trans*-**1** was recovered.

All voltammetric measurements performed in MeCN or CH_2Cl_2 were carried out with a *PAR* potentiostat Model *173* and a *PAR* universal programmer Model *175*. Cyclic voltammograms (cv) were recorded with a model *HP 7004B X-Y* recorder. A three-electrode configuration was employed throughout. Details are described in [11]. All manipulations were carried out under Ar. Potentials were calibrated with ferrocene ($E^{ox}_{1/2} = +0.352$ V *vs.* Ag/AgCl).

The electrolysis for the ESR experiment was performed in a cylindrical cell containing a helical Au anode (working electrode) and a Pt wire along the axis as the cathode [12] inside the cavity of a *Varian E-9 ESR* spectrometer.

The PM3 calculations [13] were performed on a *MicroVAX* (*Digital Equipment Corp.*) computer using MOPAC 6.00 (Quantum Chemistry Program Exchange No. 455) and ChemX (*Chemical Design Ltd.*). Restricted *Hartree-Fock* (RHF) energies were calculated from single-point calculations of the optimized UHF geometries. The calculations using PM3 semiempirical molecular-orbital theory gave better results than AM1 [14] which placed *cis*-**1** and *cis*-azomethane lower in energy than the corresponding *trans*-isomers. The adiabatic ionization potentials were calculated from the total energy (RHF) difference of $M^{+\cdot}$ and M.

Results. – Upon careful anodic oxidation (−85°; solvent: CH_2Cl_2; electrolyte: tetrabutylammonium perchlorate) or one-electron oxidation of *cis*-**1** with tris(2,4-dibromophenyl)aminium hexachloroantimonate [15] at −78° in CH_2Cl_2, an ESR spectrum identical to that of *trans*-$\mathbf{1}^{+\cdot}$ was detected. Since, on the basis of INDO calculations [10], we expect largely different coupling constants for the *cis*- and *trans*-radical cations, it is highly unlikely that by mere accident the ESR spectra of the two isomers are identical. Thus, it is plausible, that *cis* → *trans* isomerization proceeds very rapidly under electron-transfer conditions even at low temperature. While the facile *cis* → *trans* isomerization of an azo compound radical anion, *i.e.* azobenzene radical anion, has been reported in [16], a radical-cation pathway has not been mentioned to the best of our knowledge.

To study by another approach the reactivity of *cis*-$\mathbf{1}^{+\cdot}$, we have recorded the cyclic voltammograms at 0.1 $V \cdot s^{-1}$ in either CH_2Cl_2 or MeCN at different temperatures. In CH_2Cl_2, the solution of the yellow *cis*-isomer exhibited a reversible wave at $E^{ox}_{1/2} = +1.31$ V *vs.* Ag/AgCl for all temperatures, *i.e.* −40° to 20°. However, after a couple of scans over a period of few minutes at room temperature or ½ h at −40°, the *whole* solution turned colorless. While this result proposed that the *cis*-compound had completely disappeared, no significant change of the redox potential was observed ($E^{ox}_{1/2} = 1.36$ V *vs.* Ag/AgCl).

When the same experiment was carried out in MeCN as solvent ($E^{ox}_{1/2}$(*cis*-**1**) = +1.32 V *vs.* Ag/AgCl), the disappearance of the yellow color proceeded considerably slower, taking place within ½ h at room temperature. These observations are again, like the ESR results, consistent with an efficient, very rapid radical-cation chain process that isomerizes *cis*-**1** to the *trans*-isomer, not only in the diffusion layer but also in the bulk solution. The difference between the two solvents obviously results from the fact that in CH_2Cl_2 traces of HCl are present [17]. Thus, a H^+-catalyzed *cis* → *trans* isomerization, a well-documented reaction in azo chemistry [4] [5], superimposes the radical-chain process.

To obtain further information, we studied the anodic oxidation of *cis*-**1** at different scan rates by using single-sweep and multisweep techniques. In no case, a significant change of the redox potential exceeding a shift of 30 to 40 mV to more positive values was observed. In multisweep experiments at high scan rates, the small shift of the voltammetric waves results from the thermodynamically favorable *trans*-form, which is formed during the measurement (*Fig. 1*).

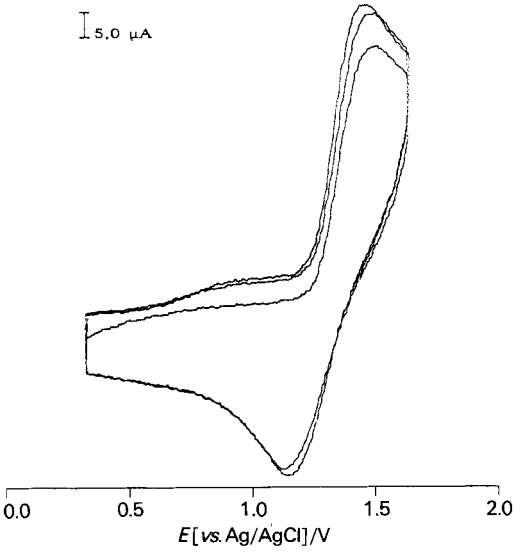
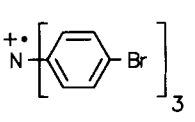


Fig. 1. *Multisweep cyclic voltammogram of* cis-**1** (10^{-3} M *cis*-**1**, 1-mm Pt electrode, v = 5 V·s^{-1}, 0.1M tetrabutylammonium hexafluorophosphate, 20°)

In consecutive single-sweep experiments, however, this change is not visible. As adsorption and filming effects can not be excluded as reasons for these shifts, we assume that the difference between the redox potentials of the *cis*- and *trans*-isomer is limited by a value of 40 to 50 mV, and that the *cis*-isomer is easier to oxidize than the *trans*-isomer. This assumption is in line with our PM3 calculations showing very similar adiabatic ionization potentials for *cis*- and *trans*-**1** (IP_a = 7.99 eV *vs.* IP_a = 8.12 eV) that compare well with the experimental vertical ionization potentials [18]. The difference in oxidation potentials for the two isomers $\Delta E^{ox}_{1/2}$ = 0.05 V and ΔH_{isom}(*cis*-**1** → *trans*-**1**) can now be used to predict *via* a simple thermochemical cycle ΔG_{isom}(*cis*-**1**$^{+\cdot}$ → *trans*-**1**$^{+\cdot}$) ≈ −67 kJ/mol, assuming that ΔS_{isom}(*cis*-**1** → *trans*-**1**) ≈ 0 e.u.

In addition, *cis*-**1** could also be isomerized by minute amounts of added tris(4-bromophenyl)aminium hexachloroantimonate (**2**) or iron(III)phenanthroline hexafluorophosphate (**3**) at room temperatur in MeCN. Both reagents are one-electron oxidants with potentials ($E^{red}_{1/2}$(**2**) = +1.10 V [19], $E^{red}_{1/2}$(**3**) = +1.13 V [20]) significantly below the one of *cis*- and *trans*-**1**. Addition of 5 mol-% of **2** to a solution of 10 mg of *cis*-**1** in 1 ml of MeCN at room temperature led to rapid decolorization of the yellow *cis*-**1** solution that was much to fast for conventional UV monitoring. Even 0.05 mol-% of **2** still isomerized *cis*-**1** within less than 3 min. Oxidant **3**, which had been shown by *Wong* and *Kochi* to behave as an outer-sphere electron-transfer reagent [20], proved to be a little bit less effective, *i.e.* addition of 0.6 mol-% of **3** resulted in a slower *cis* → *trans* isomerization with 15% *cis*-**1** still left after 15 min. UV/VIS kinetics at different concentrations of oxidant **3** showed that the reaction proceeded with first order with respect to *cis*-**1** (k_{isom} = 0.35 $M^{-1} \cdot s^{-1}$ at room temperature).



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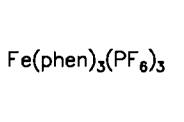

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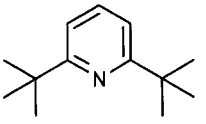

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For all the radical-cation-catalyzed isomerization reactions induced by **2** or **3**, quantitative analysis by GC and NMR showed that more than 99% of *trans*-**1** were recovered. To exclude the possibility of an acid-catalyzed *cis* → *trans* isomerization, the reactions were run in presence of 2,6-*di*(*tert*-butyl)pyridine (**4**). Up to a 10-fold excess of **4** relative to the oxidant (*i.e.* 0.03 mol-% of **2**), the time for complete isomerization was not affected. This result definitely precludes the possibility of the isomerization to proceed *via* acid catalysis.

Discussion. – Alltogether, ESR, cv, and one-electron-oxidation results are in agreement with a very efficient and rapid radical-cation-catalyzed *cis* → *trans* isomerization of **1**, which is driven by the overall high exothermicity of 68 kJ/mol.

$$cis\text{-}\mathbf{1} \overset{-e^-}{\rightleftharpoons} cis\text{-}\mathbf{1}^{+\cdot}$$

$$cis\text{-}\mathbf{1}^{+\cdot} \rightarrow trans\text{-}\mathbf{1}^{+\cdot}$$

$$trans\text{-}\mathbf{1}^{+\cdot} + cis\text{-}\mathbf{1} \rightarrow trans\text{-}\mathbf{1} + cis\text{-}\mathbf{1}^{+\cdot}$$

The small amount of oxidant needed for quantitative conversion proposes that the chain length of the isomerization is extremely high, well beyond 1000. An obvious reason for this long chain certainly is the high stability of *trans*-$\mathbf{1}^{+\cdot}$, which can be reversibly oxidized even at a scan rate v = 0.1 $V \cdot s^{-1}$ in MeCN at room temperature. Additionally, in the bridgehead azo radical-cation system, a deprotonation reaction is unlikely as there are no α-H-atoms present, and decomposition of *cis*-$\mathbf{1}^{+\cdot}$ with formation of N_2 is quite endothermic (ΔH_r = 215 kJ/mol, calculated using PM3) due to the low stability of both the norbornyl radical as well as norbornyl cation.

So far, we can only speculate about the reasons for the fast *cis* → *trans* isomerization of the radical cation. Several plausible mechanisms, *i.e. a*) rotation about the N=N bond in a π-radical cation, *b*) inversion at one N center in a σ-radical cation, or *c*) a disso-

ciation-recombination pathway *via* intermediate diazenyl cation/norbornyl radicals are conceivable, but hard to distinguish experimentally. The only mechanism, that can be excluded so far, is the dissociation-recombination mechanism, since this would require quantitative recombination of the intermediate diazenyl cations and norbornyl radicals to *trans*-**1**$^{+\cdot}$. At present, inversion around one N center in a σ-radical cation seems to be the most plausible mechanism, since both ESR data of *trans*-**1**$^{+\cdot}$ and INDO calculations on the *cis*-HN=NH radical cation [10] support the notion that *cis*-**1**$^{+\cdot}$ is also a σ-radical. This assignment could additionally be corroborated by our PM3 calculations on *cis*-**1**$^{+\cdot}$.

Some insight into the isomerization mechanism was provided by PM3 calculations on the azomethane radical-cation energy hypersurface. According to them, inversion at one N center in the σ-radical cation constitutes the minimum energy path of the *cis* → *trans* isomerization with an activation barrier of 17 kJ/mol. Both isomers are stable species, the *trans*-radical cation being more stable by 3 kJ/mol. The transition state is characterized by an almost semilinear arrangement with one C–N–N bond angle opened up to 176°, the other left at 139°. (*Fig. 2*). Interestingly, the N–N and C–N bond lengths hardly change on their way from *cis*-**1**$^{+\cdot}$ to the transition state. No stationary point for rotation about the N=N bond could be located as transition state for the isomerization process.

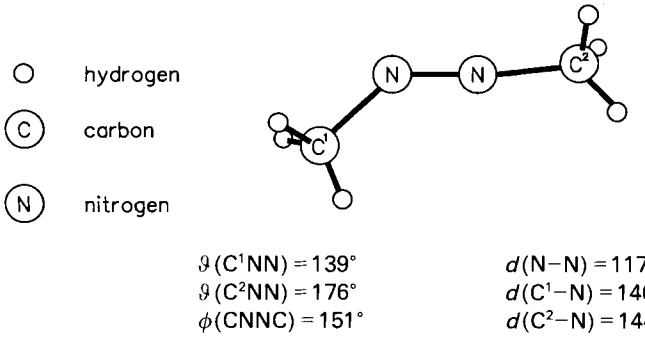

Fig. 2. *Transition-state structure for the* cis → trans *isomerization of azomethane radical cation*

Preliminary ESR studies propose that *cis*-**1**$^{-\cdot}$, too, is not configurationally stable at – 78°. Since for the anion radical the isomerization process may involve rotation about the N=N bond in a π-radical, *cis*-azonorbornane provides an interesting model system to study the various effects of both electron addition and removal on the reactivity.

For future application, the azonorbornane system constitutes a prototype of a two-stage storage system, that can be switched reversibly by photochemical *trans* → *cis* and electron-transfer-induced *cis* → *trans* isomerization. In addition, the facile *cis* → *trans* isomerization of **1**$^{+\cdot}$ may provide a probe for monitoring intermediate radical cations.

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