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# ISOMERIZATION OF THE *CIS,CIS,CIS,TRANS*-[9]ANNULENE ANION

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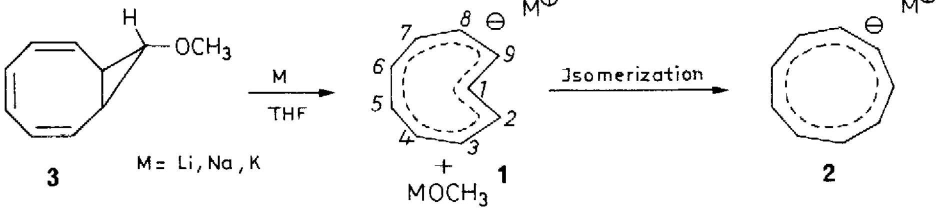
The question of conformational and configurational mobility is of central importance in annulene chemistry.[1] With *cis,cis,cis,trans*-[9]annulene anion (1) we could, for the first time, determine the conformational mobility (topomerization) of a charged annulene.[2] In this communication we report on the proton and alkali-metal catalyzed, the photochemical and the thermal isomerization of (1) to the all-*cis*-[9]annulene anion (2).



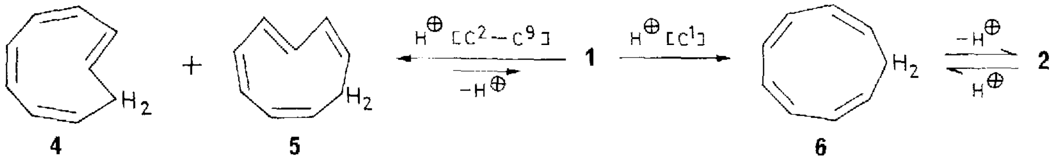
| | $M^{\oplus}$ | Solvent | Temp. [°C] | Halflife [h] | $\Delta G^{\ddagger}$ [kcal/mol] |
|---|---|---|---|---|---|
| 1 | $Li^{\oplus}$ | THF (+$LiOCH_3$) | 60 | 580 | 29.6 |
| 2 | $Na^{\oplus}$ | THF (+$NaOCH_3$) | 60 | 1200 | 30.1 |
| 3 | $K^{\oplus}$ | THF (+$KOCH_3$) | 60 | 670 | 29.7 |
| 4 | $K^{\oplus}$ | DMSO-$d_6$ | 100 | 72 | 31.6 |
| 5 | $Li^{\oplus}$/TMEDA | DMSO-$d_6$ | 100 | 200 | 32.6 |
| 6 | $Na^{\oplus}$/TMEDA | DMSO-$d_6$ | 100 | 335 | 33.0 |
| 7 | $K^{\oplus}$ | THF | 100 | 4680 | 34.8 |

Tab. 1 Isomerization of *cis,cis,cis,trans*- to all-*cis*-[9]annulene anion (1 → 2)

Table 1 gives the results of kinetic runs under different conditions.[3] In runs 1 - 3 only the excess alkali metals were removed from the otherwise crude reaction mixtures.[4] Runs 4 - 7 refer to the recrystallized salts of **1**. Run 7 is the slowest isomerization which could be measured.

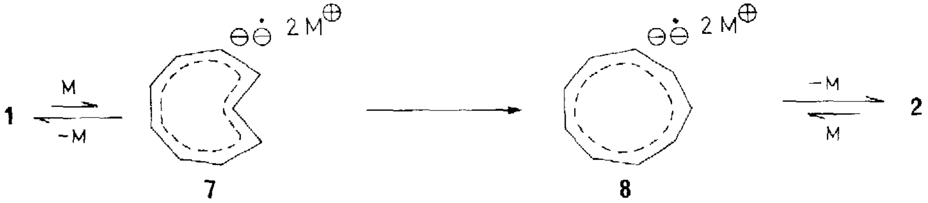
*Two features are of interest :* (a) *The isomerization to give the more stable anion* **2** requires a remarkably higher *activation energy* than the topomerization $\mathbf{1} \rightleftharpoons \mathbf{1}$ (halflife (100°C) = 0.17 sec, $\Delta G^{\ddagger}_{100^{\circ}C} = 21.1$ kcal/mol, $\Delta H^{\ddagger} = 23.6 \pm 1.5$ kcal/mol, $\Delta S^{\ddagger} = 6 \pm 8$ e.u.)[2]; (b) The $\Delta G^{\ddagger}$ values of the isomerization scatter over a wide range from 29.6 to 34.8 kcal/mol. This must be due to the fact that the isomerization $\mathbf{1} \rightarrow \mathbf{2}$ is very sensitive to catalysis.

Proton catalysis. While protonation of **1** at $C^2$ - $C^9$, giving mono-trans-cyclononatetraenes **4** and **5**[5] as intermediates, leads back to **1**, reaction at $C^1$ should generate all-cis-cyclononatetraene **6**, and thus on deprotonation the anion **2**.[6]



This is clearly demonstrated by adding 0.1 mole equiv. methanol to a solution of the potassium salt of **1** in THF at 60°C : the isomerization is 335 times faster than without methanol. In agreement with this observation, anion **2**, isolated from run 4 in DMSO-$d_6$, contained 0.41 equiv. deuterium.

Alkali metal catalysis. Compared to kinetic run 3, the isomerization of **1** is 84 times faster after addition of 10 mole equiv. potassium or Na/K alloy (1:3 molar ratio). When 2 mole equiv. caesium were used the kinetics had to be measured at -10°C. Even at this temperature the isomerization was 250 times faster than reaction 3 at 60°C without caesium ![7]

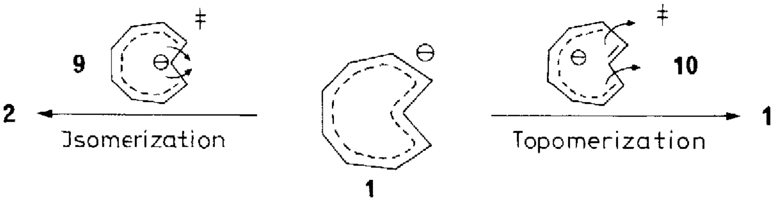


We explain this catalysis by means of a reversible electron transfer from the strong electron donating metals K or Cs to an antibonding orbital of 1 to give the dianion radical 7 ; its isomerization to the all-*cis*-isomer 8 should be much faster than the isomerization of 1. This reaction is thus analogous to the catalytic transformation of *cis*-stilbene to its *trans*-isomer by electron transfer.[8]

*Photochemical isomerization.* When a solution of the potassium salt of 1 in THF, sealed in a nmr-tube, was irradiated with a low-pressure mercury lamp (Hanau TNN 15/32) at 15°C, a halflife of the isomerization of 20 h was recorded.[9] Although this is, to the best of our knowledge, the first photochemical stereoisomerization of a carbanion and likewise of an "aromatic" (4n + 2) annulene, there exist numerous examples for reactions of this type in the photochemistry of olefins.[10]

*Thermal isomerization.* From the fact that we cannot exclude catalysis in kinetic run 7 it follows that the $\Delta G^{\ddagger}$ value of 34.8 kcal/mol can only be a lower limit value for the thermal isomerization of 1[11]. This means that at 100°C the isomerization $1 \rightarrow 2$ is at least $1.7 \cdot 10^{8}$ times slower than the topomerization $1 \rightleftharpoons 1$.

If models 9 and 10 correspond to the transition states of the isomerization and topomerization, respectively, in which rotation occurs around formal single bonds, the different activation energies can be explained as follows.



(1) Compared to the perimeter $C_9H_9^{\ominus}$, transition state 9 is 2.0 ß and transition state 10 only 1.46 ß higher in energy, according to a simple calculation of the HMO $\pi$-bond energies.

(2) At least of equal importance is the fact that in the transition state of the isomerization (9) the negative charge is localized essentially at one carbon atom, namely $C^1$. In contrast, in the transition state of the topomerization (10) the negative charge is distributed over seven carbon atoms, which clearly corresponds to a more favorable situation.

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