CIS-TRANS ISOMERIZATION OF 8-CHLOROHOMOTROPYLIUM SALTS AND OF 7,8-DICHLORO-

CYCLOOCTA-1,3,5-TRIENE

Rolf Huisgen and Johann Gasteiger

Institut für Organische Chemie der Universität, München 2, Karlstraße 23

(Germany)

The endo-8-chlorohomotropylium tetrafluoroborate ($\underline{1}$) (1), dissolved in li-
quid SO_2, rearranges in a first-order reaction quantitatively to the exo-iso-
mer $\underline{2}$. Measurements at five temperatures between 15° and 37° give the follo-
wing Eyring parameters:

$$\Delta H^{\ddagger} = 22.9 \pm 0.9 \text{ kcal·mol}^{-1}, \quad \Delta S^{\ddagger} = 3.2 \pm 3 \text{ e.u.}$$

The close correspondence with $\Delta H^{\ddagger} = 23.7 \text{ kcal·mol}^{-1}$, $\Delta S^{\ddagger} = 3.8$ e.u., found for
the isomerization of endo-8-chlorohomotropylium fluorosulfonate to the exo-iso-
mer in fluorosulfonic acid (2), suggests a nearly solvent-independent ring in-
version process.

1 endo   2 exo
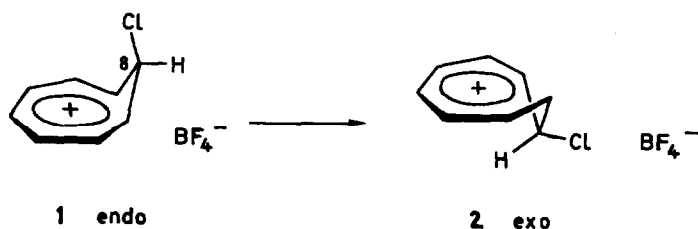
The conversion $\underline{1}$ — $\underline{2}$ is strongly catalyzed by cis-7,8-dichlorocycloocta-
triene ($\underline{4}$). In the presence of 30 mol % $\underline{4}$ a 70 : 30 mixture of $\underline{1}$ and $\underline{2}$ in SO_2
at -40° is quantitatively converted to $\underline{2}$ in 5 minutes. A Cl^- transfer mechanism
is involved here; by receiving a chloride ion from $\underline{4}$, cation $\underline{1}$ is transformed to
a new molecule of the covalent dichloride $\underline{4}$ and the original molecule of $\underline{4}$ gi-
ves rise to a new chlorohomotropylium ion. The limited stereospecificity of this
process (see below), combined with the fast ring inversion $\underline{4a} \rightleftharpoons \underline{4b}$ leads to an
isomerization $\underline{1} \rightarrow \underline{2}$.
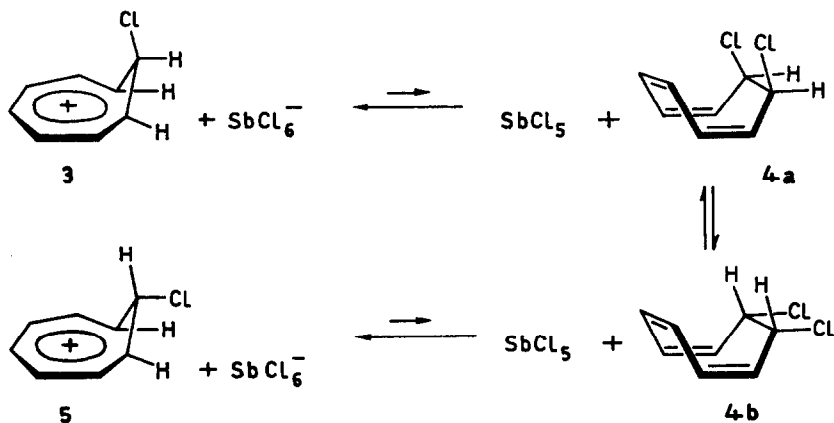
The <u>endo</u> → <u>exo</u> isomerization of the hexachloroantimonate $\underline{\underline{3}}$ in SO_2 at $15°$ is 13 times faster than the process $\underline{\underline{1}}$ → $\underline{\underline{2}}$ as shown by n.m.r. analysis. Rate measurements between $-15°$ and $+3°$ result in the following activation data:

$$\Delta H^{\neq} = 18.3 \pm 0.9 \text{ kcal·mol}^{-1}, \quad \Delta S^{\neq} = -3 \pm 3 \text{ e.u.}$$

A catalyzed path, probably the Cl^- transfer between the chlorohomotropylium ion and $SbCl_6^-$, as formulated, is superimposed on the ring inversion process $\underline{\underline{3}}$ → $\underline{\underline{5}}$.
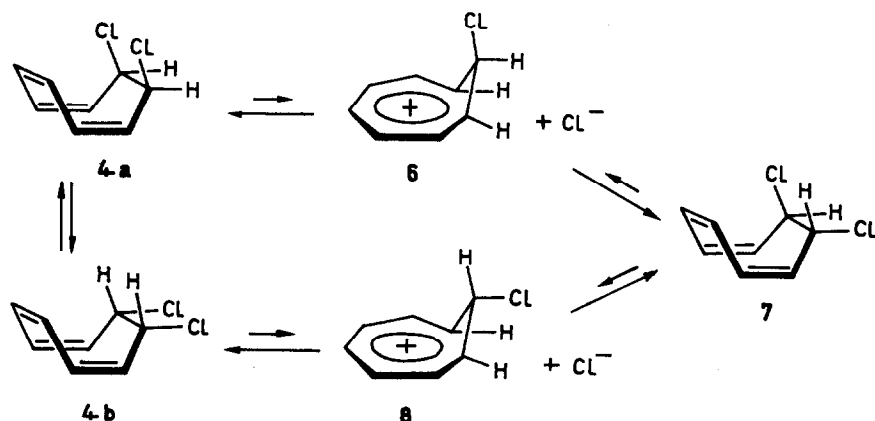
Earlier we reported that the <u>cis</u>-dichloride $\underline{\underline{4}}$ equilibrates with the <u>trans-</u> dichloride $\underline{\underline{7}}$ to form a 34 : 66 mixture in CCl_4 at $-30°$ in the presence of alumina (3). We have now found that a much smoother epimerization $\underline{\underline{4}} \rightleftharpoons \underline{\underline{7}}$ takes place in homogenous solution in SO_2 without catalyst. The table displays the results of n.m.r. spectroscopic rate and equilibrium measurements; the activation parameters refer to the step $\underline{\underline{4}}$ → $\underline{\underline{7}}$ with k_1.

Table. Rate Constants of Epimerization $\underline{4} \rightleftharpoons \underline{7}$ and Equilibria in Sulfur Dioxide

Temp. °C	% $\underline{4}$ at Equilibrium	$10^4 (k_1 + k_{-1})$ Sec^{-1}	$\Delta H^{\ddagger}$ kcal·mol^{-1}	$\Delta S^{\ddagger}$ e.u.
-22.0	34.1	4.7	12.0	-27
-17.0	34.9	7.9	± 0.8	± 3
-12.5	35.7	12.0		
- 7.5	36.5	19.2		

It is highly probable that the epimerization is effected _via_ the 8-chlo-rohomotropylium chlorides $\underline{6}$ and $\underline{8}$ as intermediates; $\underline{6}$ was shown to be formed in the primary step of the chlorination of cyclooctatetraene (4,5). The chloride ion combines stereoselectively ($\geqslant 97\%$) with the _endo_-8-chlorohomotropy-lium ion $\underline{6}$ to give the _cis_-dichloride $\underline{4}$, whereas the analogous _endo_-attack of Cl$^-$ on the _exo_-8-chloro compound $\underline{8}$ produces the _trans_-dichloride $\underline{7}$ (4,5). However, under conditions of reversible ionization and ion recombination — these are the conditions of the epimerization $\underline{4} \rightleftharpoons \underline{7}$ in SO$_2$ — thermodynamic stabilities supervene.

   Though the equilibrium concentrations of the homotropylium chlorides 6

and 8 are too small ($\leq$ 1%) to be detectable by n.m.r., the large negative acti-

vation entropy of the epimerization process (Table) is consistent with an ioni-

zation in the rate determining step and the expected electrostriction of sol-

vent molecules.

   The energy diagram summarizes the interrelationships. At $-15°$, the free

energy difference between 4 and 7 amounts to 0.3 kcal·mol^{-1} and the free ener-

gy of activation for 4 $\longrightarrow$ 7 is 18.8 kcal·mol^{-1}. The epimerization may take

place via the endo-chloride 6 or the exo-chloride 8 or, more probably, via both

6 and 8. Therefore, $\Delta G^{\neq}$ = 18.8 kcal·mol^{-1} refers to process A or B or a combi-

nation of both.

   The inversion barrier between endo- and exo-cis-dichloride 4a and 4b was

calculated from the coalescence temperature ($-35°$) of the signals for 7- and

8-H in SO$_2$: $\Delta G^{\neq}$ = 12.1 kcal·mol^{-1} (6); the conformational equilibrium in SO$_2$

at $-54°$ contains 4a and 4b in a 51 : 49 ratio. The exo-dichloride 4b contains

endo-hydrogens in the 7- and 8-positions; because of unfavorable dihedral angle

these hydrogens do not couple with 1- and 6-H and, therefore, appear as a singlet

at τ 4.81. The 7- and 8-exo-H in 4a give rise to a doublet at τ 4.56 due to coup-

ling with 1- and 6-H.

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