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THE FORMATION OF 8-SUBSTITUTED HOMOTROPYLIUM SALTS FROM CYCLOOCTA-1,3,5-TRIENE DERIVATIVES

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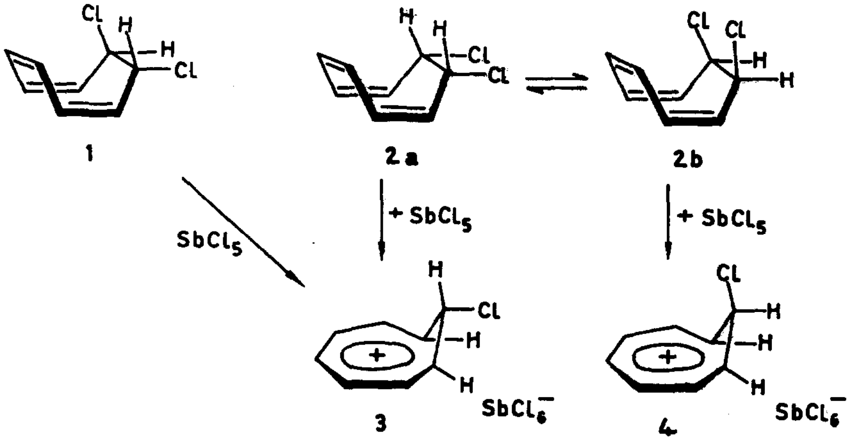
Treatment of *cis*-7,8-dichlorocyclooctatriene (2) (1) in dichloromethane with $SbCl_5$, SbF_5, $SnCl_4$ or $AgSbF_6$ is known to produce *exo*-8-chlorohomotropylium salts, whereas with fluorosulfonic acid 2 gives the *endo*-8-chlorohomotropylium salt (2). A closer investigation showed the relationships to be complicated, and the isomerizations reported in the preceding communication (3) offer a *rationale*.



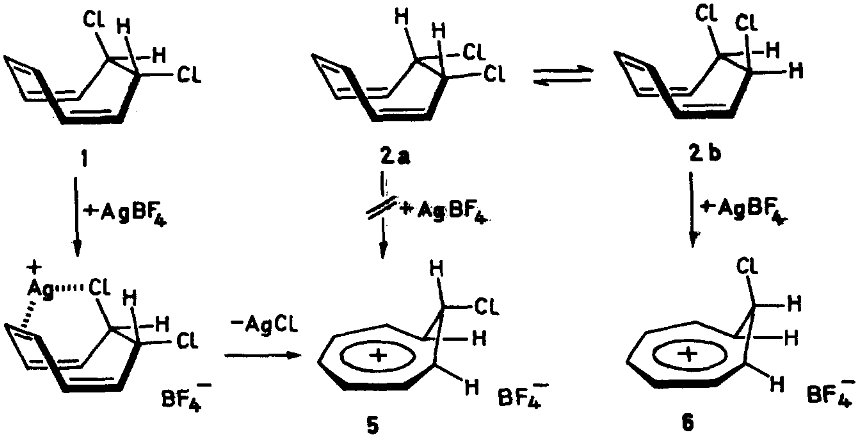
When *trans*-7,8-dichlorocyclooctatriene (1) (2) was introduced into a chloroform solution of 4 equivalents of $SbCl_5$ at -70°, a quantitative yield of the crystalline *exo*-chloro hexachloroantimonate 3 precipitated. N.m.r. analysis in SO_2 disclosed no detectable amount of the *endo*-isomer 4. Thus, the removal of the *endo*-chlorine of 1 by the Lewis acid is much faster than removal of the *exo*-Cl in **1**. This result is in accordance with the highly stereoselective *endo*-attack of Cl^- on the chlorohomotropylium ions **3** and **4** (2).

Antimony pentachloride seems to be a Lewis acid of sufficient strength to abstract chloride from the *exo*- and the *endo*-conformer of *cis*-7,8-dichlorocyclooctatriene; the equilibrium of **2a** and **2b** at -54° is 46 : 54 in dichloromethane and 49 : 51 in SO_2. Introduction of **2** into the solution of 2 equivalents of $SbCl_5$ in chloroform at -70° leads to 100% of the crystalline salts **3** and **4** in the ratio 1.0 : 1.0 (n.m.r. analysis in SO_2 at -40°). Pure *endo*-chloro hexachloroantimonate **4** has been obtained by chlorination of cyclooctatetraene with two moles of $SbCl_5$.

The *exo*- and *endo*-chloro salts **3** and **4** are virtually insoluble in chloroform, but are slightly soluble in dichloromethane. In CH_2Cl_2, dropwise introduction of **2** to a solution of 4 equivalents of $SbCl_5$ at -75° or the reverse addition resulted in pure *exo*-chloro salt **3**. We suppose that in the solution *endo*-*exo*-isomerization **4** → **3** took place, efficiently catalyzed by the covalent dichloride **2** (3), which is present for an instant at the site of mixing. In SO_2 at -75°, addition of **2** into 3 equivalents of $SbCl_5$ produced in homogenous solution ca. 10-20% of the *endo*-salt **4** along with the predominant *exo*-isomer **3** (n.m.r. analysis at -40°).

Dropwise addition of **2** in SO_2ClF to the solution of SbF_5 in the same solvent at -75° resulted in a 1:1 mixture of **3** and **4** (SbF_5Cl^- instead of $SbCl_6^-$). Thus, both conformers **2a** and **2b** are ionized by SbF_5.

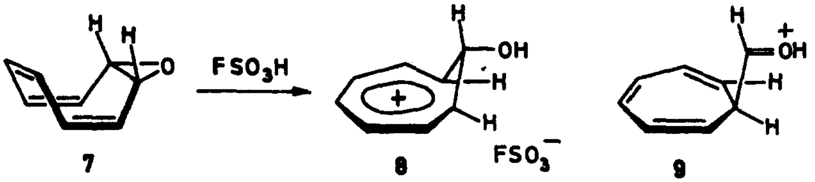
In contrast to $SbHal_5$ silver tetrafluoroborate abstracts Cl^- only from the *endo*-side of **1** and **2b**; it does not react with **2a**. The silver ion seems to be inferior to $SbHal_5$ as a Lewis acid. A primary complexation of Ag^+ with the double bond is conceivable, as illustrated in the scheme for the reaction with the *trans*-dichloride **1**, which gives the *exo*-chloro salt **5** exclusively. The same kind of assistance by the double bond is only possible in **2b**, not in **2a**.



After dropwise introduction of a solution of **2** in 1,2-dichloroethane into 2-3 equivalents of $AgBF_4$ in the same solvent at -30°, the solvent was pumped off at -20°. Extraction of the residue with SO_2 at -60° - **5** and **6** are soluble in SO_2 - and n.m.r. spectroscopy of the solution disclosed that only the endo-chloro tetrafluoroborate **6** was formed. Addition of chloroform to the SO_2 solution allowed the crystallization of **6**, m.p. 48-50° (dec., under N_2), which decomposes rapidly on exposure to air.

However, by the reverse procedure, i.e. addition of $AgBF_4$ to **2** in 1,2-dichloroethane at -30°, removal of the solvent, extraction with SO_2 at -30° and precipitation with chloroform, the exo-chloro fluoroborate **5**, m.p. 70-71°, was obtained. This salt must be handled with rigorous exclusion of air and moisture. The product of an analogous reaction, carried out in SO_2 solution at -50°, turned out to be pure **5** according to the n.m.r. spectrum. Under these conditions, an excess of **2** is present during the reaction and exerts a strong catalysis (3) of the conversion **6** → **5**.

In 1957 Ganellin and Pettit (5) postulated the 8-hydroxycycloocta-2,4,6-trienyl cation as an intermediate in the acid-catalyzed conversion of 7,8-epoxycycloocta-1,3,5-triene (**7**) to 7-formylcyclohepta-1,3,5-triene. The cationic intermediate should now be reformulated as 8-hydroxyhomotropylium ion.



The preparation of the fluorosulfonate 8 of this homoaromatic species succeeded when we condensed 7 slowly in high vacuum into stirred fluorosulfonic acid at -75°. Polymerization was minimized under these conditions. The endo-H proton signal in the n.m.r. spectrum (Fig.) leaves no doubt that the exo-8-hydroxy ion 8 was formed.

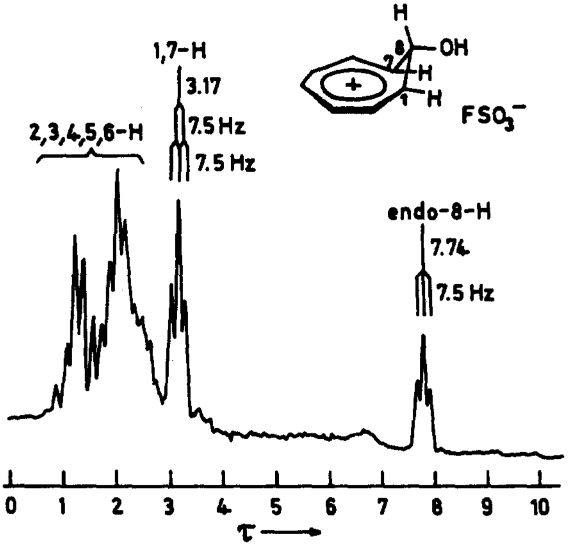


Figure. N.m.r. spectrum (60 Mc/sec) of exo-8-hydroxy-homotropylium fluorosulfonate (8) in fluorosulfonic acid at -40°.

Comparison of n.m.r. data (Table) of 8-substituted homotropylium salts with the parent compound allows some interesting conclusions. The unusually high Δτ(endo-8-H minus exo-8-H) of 5.10-5.86 ppm is the result of diamagnetic or paramagnetic shielding, respectively, by the induced homoaromatic ring current (6). The endo- oder exo-8-halogen and exo-8-OH shifts the 8-H triplet to lower field. The substituent influence corresponds qualitatively, but not quantitatively (Table 2), with the one observed in simple CH_3-X compounds (7). The low τ value of endo-8-H in **8** suggest some contribution from the hyperconjugated structure **9**.

Table 1. τ-and J-values in the 60 MHz ^{1}H n.m.r. spectra of homotropylium salts in SO_2 or FSO_3H at -40°

Reference	Homotropylium exo-8	endo-8	Anion	τ_{1+7}	τ_8 endo	τ_8 exo	J (Hz) 1,endo-8	1,exo-8	1,2
	H	H	FSO_3^-	3.57	10.73	4.87	9.8	6,5	
(4)	H	Cl	$SbCl_6^-$	3.65	-	2.73	-	6.7	6.8
	H	Cl	BF_4^-	3.67	-	2.71	-	6.8	6.8
(4)	H	Br	BF_4^-	3.66	-	2.70	-	6.9	6.9
(2)	Cl	H	$SbCl_6^-$	3.13	8.51	-	8.2	-	8.3
	Cl	H	BF_4^-	3.18	8.51	-	8.3	-	8.3
(4)	Br	H	BF_4^-	3.19	8.76	-	8.4	-	8.4
(4)	I	H	BF_4^-	3.18	9.00	-	9.3	-	8.2
	OH	H	FSO_3^-	3.17	7,74	-	7.5	-	7.5

Table 2. N.m.r. comparison between 8-exo-substituted homotropylium ions and compounds CH_3-X

	exo-OH		exo-Cl		exo-Br		exo-I		exo-H
τ(endo-8-H)	7.74		8.51		8.76		9.00		10.73
Δτ (ppm)		0.77		0.25		0.24		1.73	
	CH_3-OH		CH_3-Cl		CH_3-Br		CH_3-J		CH_3-H
τ(CH_3)	6.60		6.95		7.31		7.81		9.78
Δτ (ppm)		0.35		0.36		0.50		1.97	

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