pared by the reaction of $B_{10}H_{12}CNH_2CH_2C_6H_5$[4] with $NiCl_2$ in aqueous sodium hydroxide.

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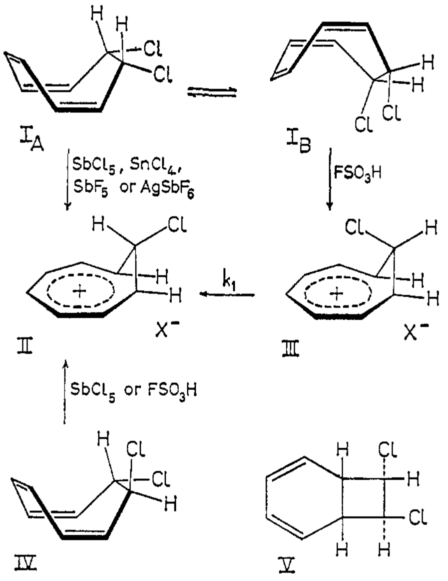
endo- and *exo*-8-Chlorohomotropylium Salts

Sir:

The occurrence of an 8-halohomotropylium ion as an intermediate in the halogenation of cyclooctatetraene is conceivable. It would explain the unique features of this reaction.[1] To provide evidence for this mechanistic possibility, we prepared *exo*- and *endo*-8-chlorohomotropylium salts. von Rosenberg, Mahler, and Pettit[2] obtained stable homotropylium salts by the reaction of cyclooctatetraene with strong acids. Further studies in the laboratories of Winstein[3] and Pettit[4] confirmed the homoaromatic character of the cationic species.

We treated *cis*-7,8-dichlorocycloocta-1,3,5-triene[5] (IA and IB) with antimony pentachloride in dichloromethane at −15° and isolated the crystalline, colorless *exo*-8-chlorohomotropylium hexachloroantimonate (II, $X^- = SbCl_6^-$) in 95% yield.[6] The salt (mp 82–85° dec in a sealed tube) is stable at room temperature but decomposes on exposure to moist air. Structural assignment is based on the nmr spectrum (CD_3NO_2).[7] The homoaromatic protons at positions 2–6 are centered at τ 1.1 (multiplet); protons 1 and 7 give rise to a triplet at τ 2.82 with $J_{12} = J_{18} = 8.2$ cps. The aromatic ring current shifts the triplet of the *endo*-8-H to τ 8.20.



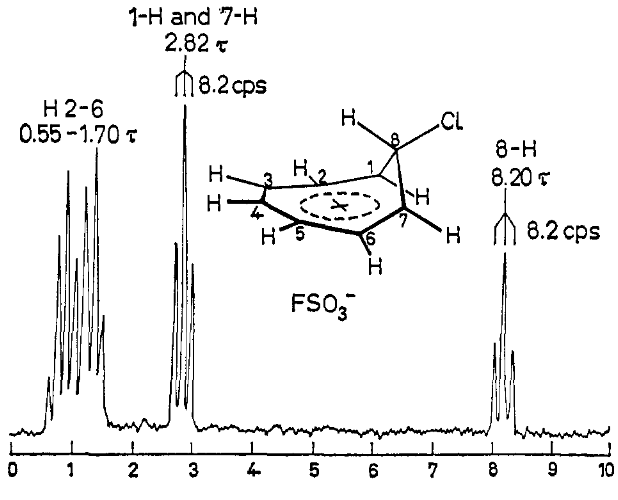


Figure 1. Nmr spectrum (FSO_3H) of *exo*-8-chlorohomotropylium fluorosulfonate at 20°.[8]

The spectrum corresponds well with that of the homotropylium hexachloroantimonate[2] after making allowance for the effect of the *exo*-8-chlorine. The spectrum of II ($X^- = FSO_3^-$) in fluorosulfonic acid (Figure 1) is very similar.

IA and IB exist at −15° in a mobile 46:54 equilibrium.[5] Besides $SbCl_5$ (in CH_2Cl_2 or SO_2), $SnCl_4$ (in CH_2Cl_2; II, $X^- = SnCl_5^-$)[6] or $AgSbF_6$ (in SO_2 or CD_3NO_2), respectively, also cause chloride elimination from the *exo,cis*-dichloride IA to give the *exo*-8-chloro cation II.

In contrast, fluorosulfonic acid attacks the *endo*-dichloro conformer IB. Treatment with ≥ 4 equiv of FSO_3H in SO_2 or with pure FSO_3H below 0° converted IB to the *endo*-8-chlorohomotropylium salt III ($X^- = FSO_3^-$). Also shown by the nmr spectrum of III (Figure 2[8]) is the equality of vicinal coupling constants, leading to two triplets, one for 1-H and 7-H, the other for 8-H. The τ value of *exo*-8-H is shifted by 5.69 to lower field compared with *endo*-8-H in II.

On warming a solution of III in FSO_3H to 30.4°, a first-order isomerization to the *exo*-chloro cation took

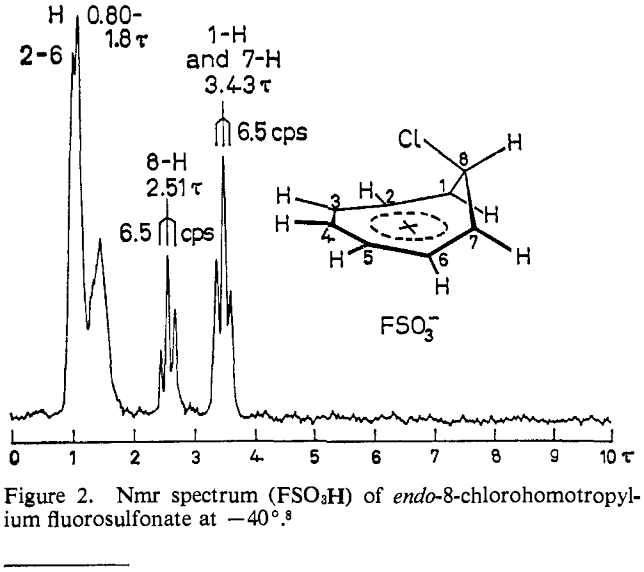


Figure 2. Nmr spectrum (FSO_3H) of *endo*-8-chlorohomotropylium fluorosulfonate at −40°.[8]

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[1] R. Huisgen, G. Boche, and H. Huber, *J. Am. Chem. Soc.*, **89**, 3345 (1967).

[2] J. L. von Rosenberg, J. E. Mahler, and R. Pettit, *ibid.*, **84**, 2842 (1962).

[3] S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *ibid.*, **87**, 3267 (1965); S. Winstein, C. G. Kreiter, and J. I. Braumann, *ibid.*, **88**, 2047 (1966).

[4] C. E. Keller and R. Pettit, *ibid.*, **88**, 604, 606 (1966).

[5] R. Huisgen, G. Boche, W. Hechtl, and H. Huber, *Angew. Chem.*, **78**, 595 (1966); *Angew. Chem. Intern. Ed. Engl.*, **5**, 585 (1966).

[6] Satisfactory carbon and hydrogen analyses were obtained.

[7] Determined on a Varian A-60 spectrometer with TMS as internal standard.

[8] TMS is destroyed by FSO_3H. Chemical shifts were corrected by using the same τ values for the two triplets as found for II ($X = SbCl_6^-$) in CD_3NO_2. For mixtures of II and III in FSO_3H, analogous corrections were applied.

place with a half-life of 37.7 min. Additional kinetic measurements (nmr) at 15.5 and 20.0° furnished values for $\Delta H^{\ddagger}$ of 24.4 kcal/mole and for $\Delta S^{\ddagger}$ of 3.8 eu. The *exo*-chloride II, probably formed by ring inversion of the *endo*-chloride III, is the thermodynamically stable isomer since no III is detectable after complete isomerization. $SbCl_5$ does not catalyze the process III → II. Winstein, *et al.*,[3] found a half-life of 19 min for the equilibration of the *endo*-8-*d*-homotropylium ion in D_2SO_4 at *ca.* 32°.

On treating *trans*-7,8-dichlorocyclooctatriene[5] (IV) with $SbCl_5$ in dichloromethane at −20°, the *exo*-chloro salt II precipitated. The same reaction in SO_2 at −40° resulted in a solution of which the nmr revealed solely the presence of II. Interestingly, fluorosulfonic acid at −20° converted IV to the same *exo*-chloro cation II. Thus, in the ionizations of I and IV, induced by FSO_3H, the chloride anion is removed from the *endo* side, while $SbCl_5$ gives in both cases the more stable *exo*-chloro cation. The origin of this dichotomy —all ionizations described above are unidirectional and kinetically controlled—is unknown.

Reppe's dichloride V[9] is not transformed to a homotropylium salt by FSO_3H.

[9] W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Ann. Chem.*, **560**, 1 (1948).

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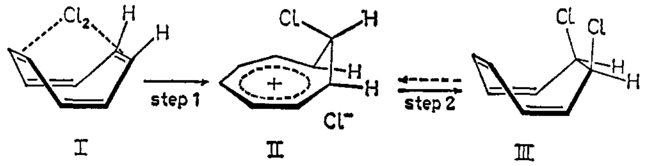
The Halogenation of Cyclooctatetraene *via* 8-Halohomotropylium Ions

Sir:

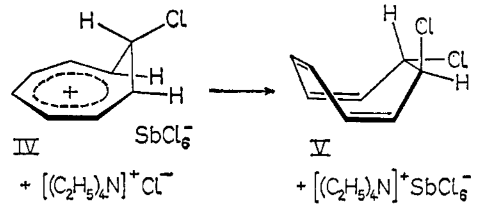
The 7,8-*trans*-dihalobicyclo[4.2.0]octa-2,4-dienes which Reppe, *et al.*,[1] obtained from cyclooctatetraene and halogen are the result of multistep reactions.[2,3] In the chlorination, we isolated four isomeric dichlorides and elucidated their structures as well as their mutual relationships.[3] The halogenation shows several unique features: (1) exclusive primary *cis* addition over the solvent range from hexane to acetonitrile; (2) unusually high rate; in the bromination at −55°, the solution remains colorless until the first drop of bromine exceeds 1 mole equiv; (3) the *cis*-7,8-dihalocycloocta-1,3,5-trienes isomerize readily to the *trans* isomers despite steric hindrance of allylic resonance in the tub form.

We propose [8-halohomotropylium cation (II) as an intermediate. The formation of this homoaromatic species would obviously explain the high rate of halogenation. This being the case, both steps of Scheme I, formulated for chlorination, should take place highly stereoselectively. Experimental evidence on step 2 is easily accessible.

Scheme I



Step 2. We added 1.1 equiv of tetraethylammonium chloride to *exo*-8-chlorohomotropylium hexachloroantimonate (IV)[4] in SO_2 at −40° and recorded the nmr spectrum of the clear solution. Signals[5] were observed indicating the presence of only *trans*-7,8-dichlorocyclooctatriene (V).[3] Thus, the chloride anion approaches C-1 from the *endo* side.



cis-Dichloride III (2.6 mmoles) was treated with 10 mmoles of fluorosulfonic acid in 6 ml of SO_2 at −20° to give pure *endo*-8-chlorohomotropylium salt (II, FSO_3^- instead of Cl^-).[4] After 5 min, 15 mmoles of tetraethylammonium chloride was introduced. The nmr spectrum of the clear solution (−40°, after 10 min) indicated 94% *cis*-dichloride III and 6% *trans* isomer V. The formation of the small amount of V is most likely not due to kinetic, but rather to thermodynamic, control.[6] Thus, both homotropylium ions suffer *endo* attack by the nucleophilic Cl^-.

Step 1. Only the *endo*-chlorohomotropylium ion II is consistent with the quantitative formation of the *cis*-dichloride III in the chlorination of cyclooctatetraene. Conclusive evidence for the high stereoselectivity of step 1 (I → II) is not available because with no known chlorinating reagent can the reaction be terminated reliably at the cationic stage II. We assume that $Cl_2\cdots SbHal_5$ chlorinates faster than Cl_2 and gives directly 8-chlorohomotropylium hexachloroantimonate. In the reactions with Cl_2 and *$SbCl_5$* in dichloromethane, the hexachloroantimonates II ($SbCl_6^-$ instead of Cl^-) and IV precipitated and were weighed and analyzed by nmr in SO_2 at −40°. The use of Cl_2 and *SbF_5* permitted direct nmr analysis of the clear reaction solutions.

The data of Table I reveal that the yield of *endo*-8-chlorohomotropylium salt rises with decreasing reaction temperature and increasing concentration of $SbHal_5$; SbF_5 appears to be more efficient than $SbCl_5$.

Table I. Reactions of Cyclooctatetraene with 1.0 Equiv of Cl_2 and $SbHal_5$ in Dichloromethane

Equiv of $SbHal_5$	Temp, °C	% hexahaloantimonate II and IV	*endo*-Cl(II): *exo*-Cl(IV)
1.2 $SbCl_5$	−20	75	17:83
4.0 $SbCl_5$	−20	78	47:53
1.2 $SbCl_5$	−93	77	50:50
3.0 $SbCl_5$	−93	76	62:38
2.0 SbF_5[a]	−50	(100)	66:34
1.2 SbF_5[a]	−93	(100)	56:44

[a] Solvent: CH_2Cl_2–SO_2.

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[1] W. Reppe, O. Schlichting, K. Klager, and T. Töpel, *Ann. Chem.*, **560**, 1 (1948).

[2] R. Huisgen and G. Boche, *Tetrahedron Letters*, 1769 (1965).

[3] R. Huisgen, G. Boche, W. Hechtl, and H. Huber, *Angew. Chem.*, **78**, 595 (1966); *Angew. Chem. Intern. Ed. Engl.*, **5**, 585 (1966).

[4] G. Boche, W. Hechtl, H. Huber, and R. Huisgen, *J. Am. Chem. Soc.*, **89** 3344 (1967).

[5] The limit of nmr analysis of the *cis* isomer III in the presence of a large amount of V is *ca.* 6%.

[6] Uncatalyzed isomerization of the *cis*-dichloride III in SO_2 at −40° led to 15% V after 30 min and to 40% V after 5 hr.