place with a half-life of 37.7 min. Additional kinetic measurements (nmr) at 15.5 and 20.0° furnished values for $\Delta H^{\pm}$ of 24.4 kcal/mole and for $\Delta S^{\pm}$ 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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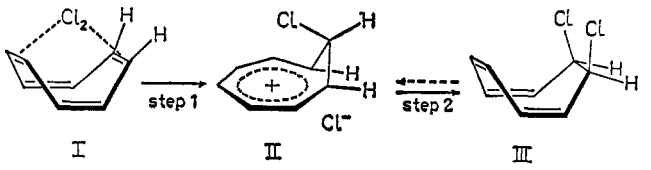
The Halogenation of Cyclooctatetraene *via* 8-Halohomotropylium Ions

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.

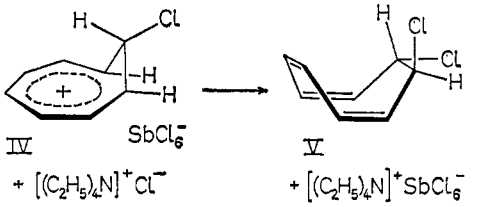
We propose β-halohomotropylium cation (II) as an intermediate. The formation of this homoaromatic species would obviously explain the high rate of halogenation. This being the case, both steps of Scheme I, formulated for chlorination, should take place highly

Scheme I



stereoselectively. Experimental evidence on step 2 is easily accessible.

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.

(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.

$$Cl_2 + SbHal_5 \rightleftharpoons \overset{\delta^+\ \ \delta^-}{Cl{-}Cl}\cdots SbHal_5$$
VI

We interpret these results as concurrent chlorinations by Cl_2 and reagent VI. The former yields the *cis*-dichloride III which is converted in a second step by $SbHal_5$ to give pure *exo*-chloro cation IV.[4] The *endo-chloro cation* II ($SbHal_6^-$ instead of Cl^-) *can therefore only be the result of a direct attack of the complex VI on cyclooctatetraene.* Consistent with this interpretation is the dependence of the ratio II:IV on temperature and $SbHal_5$ concentration; this substantiates the conclusion that the primary step of chlorination is the formation of the *endo*-chloro cation II.

On treating cyclooctatetraene with D_2SO_4 at $-10°$, Winstein, *et al.*,[7] obtained *endo*- and *exo*-8-*d*-homotropylium salt in an 80:20 ratio. Our experiments with FSO_3D at $-70°$ gave a 75:25 product ratio. The virtually quantitative formation of III in the chlorination requires a more specific *endo* attack of "Cl^+" on cyclooctatetraene than in the deuteration. Possibly, initial formation of the π-complex I contributes to the high stereoselectivity observed.

cis–trans **Isomerization.** A 66:34 equilibrium of dichlorides V:III is established in CCl_4 at $-30°$ in the presence of alumina.[3] The isomerization III → V in SO_2 at $-40°$ [6] is accelerated by catalytic amounts of *p*-toluenesulfonic or fluorosulfonic acid. These observations are also highly suggestive of 8-chlorohomotropylium ions as intermediates. Since ring inversion of *endo*- and *exo*-chloro cation II → IV does not take place at $-30°$,[4] ionization of dichlorides III and V and or Cl^- attack on 8-chlorohomotropylium ions II and IV is, therefore, not absolutely stereospecific.

Inspection of models leaves no doubt that the π overlap between the orbitals at positions 1 and 7 of the homotropylium ion is substantially larger on the underside than on the side of the C-8 bridge. This may be the principal reason for the *endo* attack in both steps of Scheme I.

(7) S. Winstein, C. G. Kreiter, and J. I. Braumann, *J. Am. Chem. Soc.*, **88**, 2047 (1966).

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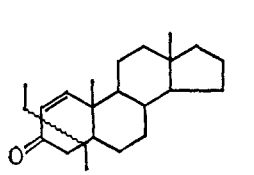
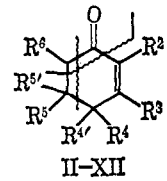
On the Mechanism of Electron Impact Induced Elimination of Ketene in Conjugated Cyclohexenones and Correlations with Photochemistry[1,2]

Sir:

It is of significant mechanistic concern to note that, upon electron bombardment of certain molecules containing the 2-cyclohexenone moiety,[3–6] a neutral species is eliminated containing the elements[3] of ketene which would formally require the energetically unfavorable[7,8] scission of a vinylic bond, *e.g.*, in Δ^1-5α-androsten-3-one (I).


I


II–XII

The extent of ketene elimination in the fragmentation of a series of methyl-substituted cyclohexenones is presented in Table I. The loss of ketene (defined by deuterium labeling[9] and high-resolution mass spectra[10]) is prominent in the decomposition of only those compounds which have at least one methyl substituent at C-4. The steroids and bicyclic enones I, $\Delta^{1(9)}$-4-methyl-2-octalone (XIII), $\Delta^{1(9)}$-10-methyl-2-octalone (XIV), *trans*-Δ^3-9,10-dimethyl-2-octalone (XV), *cis*-Δ^3-9,10-dimethyl-2-octalone (XVI), 8-methyl-$\Delta^{4(9)}$-tetrahydroindan-5-one (XVII), and Δ^4-cholesten-3-one (XVIII), from which ketene is eliminated on electron impact, also fulfill the minimum requirement of a substituent at the carbon γ to the carbonyl group.

Table I. Loss of Ketene from 2-Cyclohexenones[a]

Compound	Mass M − C_2H_2O	% Σ_{39} M − C_2H_2O	Relative intensity M − CHO	Relative intensity M − C_2H_4
II, R^2–R^6 = H	54	0.61	2	100
III, R^2 = CH_3	68	0.95	1	100
IV, R^2, R^3 = CH_3	82	<0.80	3	100
V, R^3 = CH_3	68	0.41	1	100
VI, R^3, R^4 = CH_3	82	4.69	21	100
VII, R^4 = CH_3	68	6.72	34	100
VIII, R^4, $R^{4'}$ = CH_3	82	15.92	100	90
IX, R^5, $R^{5'}$ = CH_3	82	<0.94	2	100
X, R^3, R^5, $R^{5'}$ = CH_3[b]	96	<0.33	2	100
XI, R^6 = CH_3[c]	54	<0.56	1	100
XII, R^4, $R^{4'}$, R^6 = CH_3[c]	82	4.27	20	100

[a] Values are calculated from complete high-resolution spectra for all compounds except IV, IX, X, and XI. All R = H unless otherwise specified. [b] J. H. Bowie, *Australian J. Chem.*, **19**, 1619 (1966). [c] See ref 10.

A related minimal structural requirement has been established for the photoinduced rearrangement in *t*-butyl alcohol of cyclohexenone derivatives to the bicyclo[3.1.0]hexan-2-one system; *i.e.*, two alkyl substituents are required at C-4 before rearrangement of the type VIII to XIX is observed.[11] This similarity in minimal structural requirements is suggestive that,

(1) Part XIII: High-Resolution Mass Spectrometry in Molecular Structure Studies; for part XII, see D. H. Smith, H. K. Schnoes, and A. L. Burlingame, in preparation.

(2) This research was supported in part by the National Aeronautics and Space Administration, Grant NsG 101, and Public Health Service Grant No. AM-709, National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service.

(3) Previous experimenters have employed deuterium labeling to confirm the origin and identity of the specific atoms involved in the formation of ketene. See R. H. Shapiro, J. M. Wilson, and C. Djerassi, *Steroids*, **1** 1 (1963); H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, pp 155–159.

(4) V. I. Zaretskii, N. S. Wulfson, and V. L. Sadovskaya, *Tetrahedron Letters*, 3879 (1966).

(5) M. Audier, M. Fetizon, and W. Vetter, *Bull. Soc. Chim. France*, 415 (1964).

(6) R. H. Shapiro and C. Djerassi, *J. Am. Chem. Soc.*, **86**, 2825 (1964).

(7) L. Ahlquist, R. Ryhage, E. Stenhagen, and E. von Sydow, *Arkiv Kemi*, **14**, 211 (1959).

(8) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 98–99, 328–330.

(9) M. Senn, W. J. Richter, and A. L. Burlingame, *J. Am. Chem. Soc.*, **87**, 680 (1965).

(10) In the case of C-6 substituted compounds the peak occurs at M − (41 + R_6).

(11) W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, unpublished observations.