$$Cl_2 + SbHal_5 \rightleftharpoons \overset{\delta^+\ \ \delta^-}{Cl{-}Cl}\cdots SbHal_5$$
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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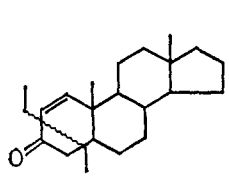
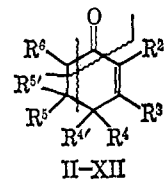
On the Mechanism of Electron Impact Induced Elimination of Ketene in Conjugated Cyclohexenones and Correlations with Photochemistry[1,2]

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).

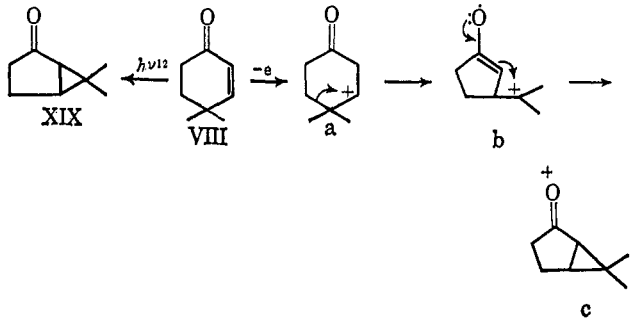
(8) K. Biemann, "Mass Spectrometry," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 98–99, 328–330.

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

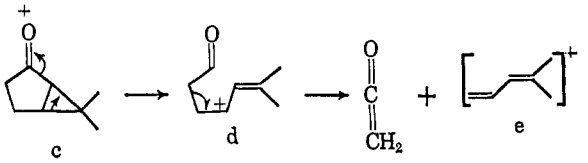
(10) In the case of C-6 substituted compounds the peak occurs at M − (41 + R_6).

(11) W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, unpublished observations.

before fragmentation occurs in the vibronically excited state, a rearrangement of some of the molecular ions of VIII occurs to molecular ion c, formally analogous to that of compound XIX, the photoisomer derived from the enone VIII. One pathway by which



the ketene could be lost would be the subsequent fragmentation of this rearranged molecular ion c.



In the high-resolution mass spectrum of the bicyclic photoproduct XIX, the ion formed by elimination of ketene from the molecular ion makes the major contribution (% Σ_{39} 27.47) to the total ion current. The loss of C-2 and C-3 is confirmed in the spectrum of 6,6-dimethylbicyclo[3.1.0]hexan-2-one-3,3-d_2. It appears (see Figures 1 and 2) that the enone VIII generates a hydrocarbon fragmentation pattern primarily *via* loss of ketene and an oxygen fragmentation pattern by loss of ethylene. Decomposition of the bicyclic-[3.1.0] ketone XIX generates a strikingly similar hydrocarbon fragmentation pattern. Thus, 4,4-dimethyl-2-cyclohexenone may be another example in which rearrangement or fragmentation observed on photon absorption also occurs on electron impact.[13-16]

However, two points remain unexplained in this analogy to the photorearrangement. (a) Compounds I, VI, VII, and XIII, which do lose ketene on electron impact, have been observed not to rearrange on irradiation to the bicyclo system. (b) In addition, comparison of the mass spectrum of cholestenone's photoproduct[17] with that of cholestenone indicates that the "photorearrangement" cannot be the major path under electron impact leading to loss of ketene from cholestenone.

Nonetheless, the bicyclo[3.1.0] system remains an attractive and reasonable general intermediate from which to lose ketene. The bicyclo[3.1.0] system could be generated by any of several bond migrations in the cyclohexenone molecular ion, including the "photorearrangement" VIII → b. Migration to C-3 of a

(12) O. L. Chapman, T. A. Rettig, A. I. Dutton, and P. Fitton, *Tetrahedron Letters*, 2049 (1963).
(13) F. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959).
(14) N. J. Turro, D. C. Neckers, P. A. Leermakers, D. Seldner, and P. D. Angelo, *J. Am. Chem. Soc.*, **87**, 4097 (1965).
(15) P. Brown, J. Kossanyi, and C. Djerassi, *Tetrahedron Suppl.*, [I] **8**, 241 (1966).
(16) After submission of this manuscript, Professor Carl Djerassi of Stanford University informed us that similar observations had been recorded in his laboratory but with a different interpretation. See R. L. N. Harris, F. Komitsky, Jr., and C. Djerassi, *J. Am. Chem. Soc.*, in press.
(17) B. A. Shoulders, W. W. Kwie, W. Klyne, and P. D. Gardner, *Tetrahedron*, **21**, 2973 (1965).

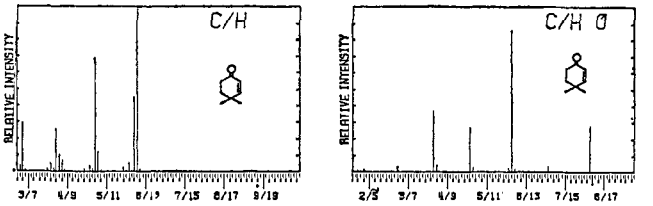


Figure 1. The complete high-resolution mass spectrum of 4,4-dimethylcyclohex-2-enone.

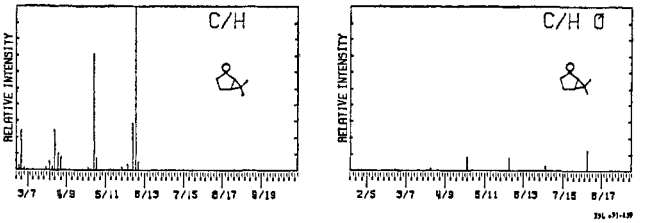
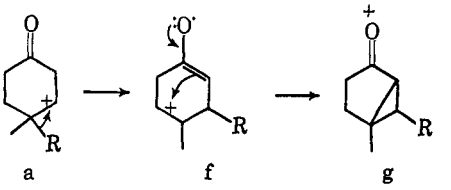


Figure 2. The complete high-resolution mass spectrum of 7,7-dimethylbicyclo[3.1.0]hexan-2-one.

methyl group from C-4[16] as shown in a → f could lead to formation of the ionized bicyclo[3.1.0]hexane-2-one derivative (f → g) in a manner analogous to that postulated in b → c. In polycyclic systems three different alkyl migrations are possible from the quaternary center γ to the carbonyl group. In VII and XIII



migration of the tertiary γ-hydrogen atom could also lead to a bicyclo[3.1.0]hexan-2-one (a → g). The suggestion is made, then, that ketene is lost from cyclohexenone derivatives through a rearranged bicyclo-[4.1.0]hexan-2-one system, whose formation requires one or another bond migration from the substituted γ carbon.

The structural features reported above are necessary for the loss of ketene from conjugated cyclohexenones, although reports indicate that the relative importance of this elimination may be altered by the presence of additional functional groups[18] and, in the rigid steroid systems, by different stereochemistry.[19]

Acknowledgment. We wish to thank Mr. B. Simoneit and Mr. D. H. Smith for determination of the high-resolution mass spectral data.

(18) S. H. Eggers, *Tetrahedron Letters*, 733 (1965).
(19) H. Egger, *Monatsh.*, **97**, 1290 (1966).
(20) (a) Hoffmann-LaRoche Company, Basel, Switzerland; (b) Public Health Service Predoctoral Fellow, 1965–1967.

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Intramolecular Migration of Tritium and Deuterium during Nonenzymatic Aromatic Hydroxylation

Sir:

It has recently been discovered that during enzymatic hydroxylation of aromatic substrates the substituent