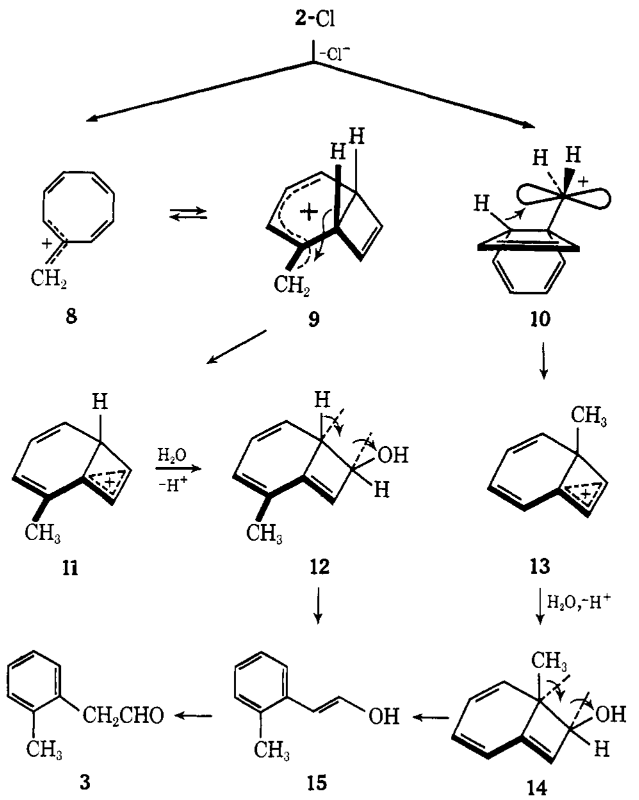
Scheme I



We note, however, that the valence isomerization of cyclooctatetraene to bicyclo[4.2.0]octatriene must overcome $\Delta H^{\ddagger} = 27$ kcal/mol, a barrier height which depends little on ring substitution.[6a,10] The low activation enthalpy for hydrolysis of 2–Cl (20.7 kcal/mol) seemingly excludes the incursion of those pathways initiated by valence isomerization. Before final acceptance of **8** as the sole intermediate of mechanistic consequence, however, supportive data in the form of isotopic labeling studies and results realized from independent generation of **8** are, of course, needed. Work along these lines is currently in progress.

Notwithstanding, the driving force underlying the generation of cation **11** undoubtedly stems from the highly stabilized nature of homocyclopropenium cations.[11] The absence of overt anchimeric assistance in 2–Cl can be traced to the folded nature of the π system in **8** which is adequate to misalign the p orbitals sufficiently to generate a measurable level of inductive rate retardation.[12]

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carbonium ions occur with an activation energy of 8.5 kcal/mol, while 1,4-hydride shifts are only slightly more demanding (12–13 kcal/mol).

(10) E. Vogel, H. Kiefer, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964); *Angew. Chem., Int. Ed. Engl.*, **3**, 442 (1964); R. Huisgen and F. Mietzsch, *Angew. Chem.*, **76**, 36 (1964); *Angew. Chem., Int. Ed. Engl.*, **3**, 83 (1964).

(11) T. J. Katz and E. H. Gold, *J. Amer. Chem. Soc.*, **86**, 1600 (1964).

(12) J. C. Martin and B. R. Ree, *J. Amer. Chem. Soc.*, **92**, 1660 (1970); V. Buss, R. Gleiter, and P. v. R. Schleyer, *ibid.*, **93**, 3927 (1971).

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[8]Annulene as a Neighboring Group. II. Response of the Cyclooctatetraene Ring to Homoallylic Electron Deficiency[1]

Sir:

An interesting contrast in reactivity is found in the susceptibility of cyclooctatetraene (COT) and benzene to electrophilic attack. Owing to the lack of significant resonance stabilization in COT and its conversion under such conditions to stabilized homotropylium cations, its ease of protonation far exceeds that of benzene which is transformed to the benzenonium cation. Despite the energy disadvantage associated with the latter process, β-phenethyl derivatives do solvolyze by way of σ-bridged phenonium ions. However, the latent potential of COT to function as a like neighboring group, perhaps with formation of related homotropylium ions, has not been examined. We now describe a novel series of rearrangements which operates upon ionization of β-COT ethyl derivatives.

Lithiation of BrCOT followed by reaction with ethylene oxide gave **1**–OH (OPNB, mp 79–81°; ODNB, mp 69–70°;[2] OBs, mp 41–42°).[3] The solvolytic reactivity of **1**–OBs in buffered acetic acid, the data for which are summarized in Table I, clearly is allied more closely to the behavior of the fully saturated **2**–OBs than to that of **3**–OBs. Good first-order kinetic behavior was noted in all three cases. When solvolyzed for ten half-lives at 85°, **2**–OBs afforded only **2**–OAc. Acetolysis (50°) of **3**–OBs under highly buffered conditions (tenfold molar excess of NaOAc) led to the formation of **3**–OAc (34%), **4** (55%), and **5** (10%);[4] the structures of these products were confirmed by independent synthesis. Reduction in the amount of buffer and increased temperatures favored enhanced conversion to **3**–OAc as well as to small amounts of unidentified elimination products.[5]

Table I. Buffered (NaOAc) Acetolysis Rate Data

Brosylate	Temp, °C	k_1, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Rel rate, 65°
1–OBs	55.00 ± 0.02	1.91×10^{-6}			
	65.00 ± 0.03	6.58×10^{-6}	25.3	−7.9	5
	75.00 ± 0.03	1.87×10^{-5}			
2–OBs	65.0	1.43×10^{-6} [a]			
	75.00 ± 0.03	4.69×10^{-6}	24.9	−11.8	1
	85.00 ± 0.03	1.16×10^{-5}			
	95.00 ± 0.03	3.25×10^{-5}			
3–OBs	45.00 ± 0.02	3.43×10^{-5}			
	55.00 ± 0.03	1.25×10^{-4}	24.9	−0.78	260
	65.00 ± 0.03	3.74×10^{-4}			

[a] Extrapolated value based on activation parameters.

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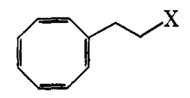
(1) Part I: L. A. Paquette and K. A. Henzel, *J. Amer. Chem. Soc.*, **95**, 2724 (1973).

(2) A. C. Cope and D. F. Rugen, *J. Amer. Chem. Soc.*, **75**, 3215 (1953).

(3) Satisfactory (±0.3%) elemental analyses and spectra compatible with the structural assignments were obtained for all new compounds reported herein.

(4) Roughly comparable results have been realized previously from deamination of 3–NH₂ and hydrolysis of 3–OTs: M. Hanack, H. Schneider-Berlohr, H.-J. Schneider, R. Huttinger, and G. Wentrup, *Justus Liebigs Ann. Chem.*, **717**, 41 (1968).

(5) As might be expected, **3**–OAc was stable to the reaction conditions. In contrast, **4** underwent partial conversion to **3**–OAc and **5** (4:1), while **5** isomerized exclusively to **3**–OAc. One of the elimination products has been identified as 2-ethyl-1,3-cyclooctadiene.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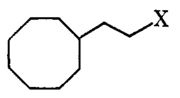
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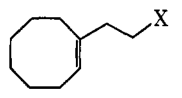
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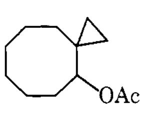
Similar acetolysis (75°) of **1**–OBs resulted in conversion to **1**–OAc, **6**–OAc, and, at low buffer concentrations, 1,2-dihydronaphthalene (**7**), naphthalene (**8**), and tetralin (**9**). Evidence gathered from several runs has denoted a significant variation in product ratio as a function of NaOAc concentration (Table II). Moreover, independent treatment of **6**–OAc with *p*-toluenesulfonic acid in acetic acid causes almost total conversion to **7**. Accordingly, we advance the tentative suggestion that **6**–OAc and **7** arise from a common reactive intermediate with formation of **6**–OAc being favored in a medium containing high levels of acetate ion. The structural elements inherent in **6**–OAc are founded upon suitable chemical correlation with *cis*-perhydro-1-azulenone (semicarbazone, mp 220–221°)[6] as well as detailed spin decoupling and Eu(fod)$_3$ shifting of the nmr spectrum of **6**–OH obtained by hydride reduction.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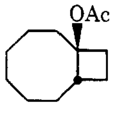
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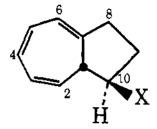

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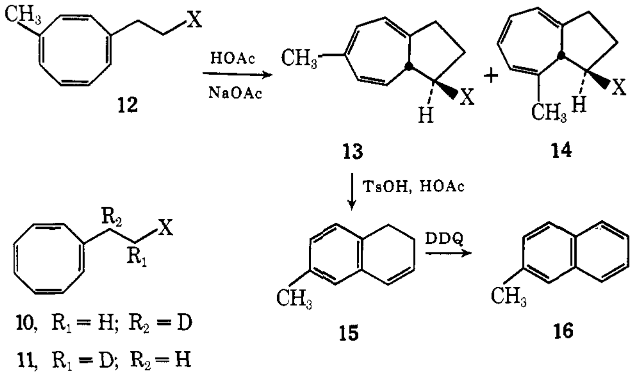
Table II. Product Variation during Acetolysis of **1**-OBs

Run	Molar proportion, NaOAc	Concn, *N*	Product composition, %: 1-OAc	6-OAc	7	8	9
A	1	0.1			86	7	7
B	10	0.2	19	69	12		
C	10	2.0	49	48	3		

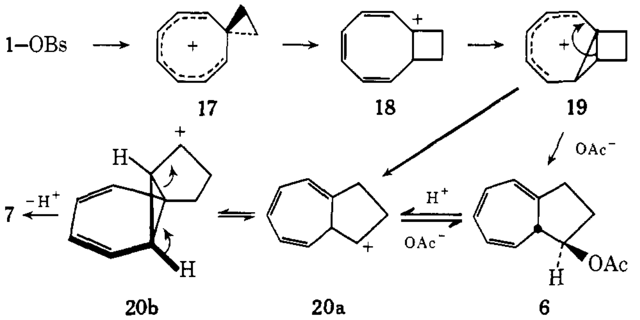
That the precursors to **1**–OAc and **6**–OAc are nonidentical was revealed upon acetolysis of **10**–OBs and **11**–OBs.[7] In both instances, the unrearranged acetates were found *not* to have undergone deuterium scrambling. Their genesis may therefore be simply accounted for in terms of S$_N$2 behavior. As regards formation of labeled **6**–OAc, the deuterium was found to be distributed equally between C$_8$ and C$_9$, irrespective of the β-COT ethyl-d_2 precursor.[8] The isolated 1,2-dihydronaphthalenes were also equitably isotopically substituted at C$_1$ and C$_2$.[8] That the carbonium ion precursor to **6** (and also **7**) must be symmetrical was substantiated further by the behavior of **12**–OBs. Prepared admixed with the 1,5 isomer by bromination–dehydrobromination of MeCOT,[9] halogen–metal exchange (*n*-BuLi), and condensation with ethylene oxide, **12**–OH was obtained by vpc isolation from a 5% Carbowax–1% KOH column (140°). Reaction of **12**–OH with Fe$_2$(CO)$_9$ and esterification of the complex with *p*-nitrobenzoyl chloride in pyridine gave a crystalline Fe(CO)$_3$ derivative (mp 82–83°), three-dimensional X-ray analysis of which unequivocally established the 1,4 placement of substituents.[10] The solvolysis of **12**–OBs gave an inseparable mixture of **13**–OAc and **14**–OAc (*ca.* 1:1, 80%) together with **12**–OAc (20%) and a trace of a methyldihydronaphthalene. Acetates **13**–OAc and **14**–OAc were characterized by spectral analysis preceding (as a mixture) and subsequent to hydride reduction, trimethylsilylation, vpc separation, and hydrolysis to individual alcohols. Additionally, the acid-promoted rearrangement of **13**–OH exclusively to **15** substantiates the assignment. Under these conditions, **14**–OH does not aromatize as expected (see below).



10, R$_1$ = H; R$_2$ = D
11, R$_1$ = D; R$_2$ = H

The intriguing rearrangement of **1**–OBs and its congeners (**10**–**12**–OBs) to tetrahydroazulenoid products as delineated above imposes a number of mechanistic limitations which are satisfied by Scheme I.

Scheme I



As required by the data, the homoallyl–cyclopropylcarbinyl interconversion[11] which leads to **17** eventuates in simultaneous symmetrization of both the ring and side chain. Whether **17** partakes of homoaromatic delocalization remains presently an open question which we are actively investigating. Passage to cyclobutyl cation **18**[11] triggers bond relocation, presumably *via* the strained **19**,[12] thereby providing access to the cycloheptatrienylcarbinyl–norcaradienylcarbinyl pair **20a** and **20b**. At high acetate ion concentrations, **20** (and possibly also **19**) experiences charge annihiliation with formation of **6**–OAc. When the acetate levels are

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[6] C. D. Gutsche, I. Y. C. Tao, and J. Kozma, *J. Org. Chem.*, **32**, 1782 (1967).

[7] Alcohol **10**–OH was prepared by LiAlD$_4$ reduction of COT-CH$_2$CO$_2$CH$_3$. The synthesis of **11**–OH consisted in deuterium exchange (NaOCH$_3$, CH$_3$OD) of this ester and subsequent LiAlH$_4$ reduction.

[8] These analyses were accomplished by nmr methods and isotope effects have not been taken into consideration.

[9] W. E. Konz, W. Hechtl, and R. Huisgen, *J. Amer. Chem. Soc.*, **92**, 4104 (1970).

[10] J. Clardy, personal communication. We thank Professor Clardy for advance information concerning this structural work, full details of which will appear in our full paper on the title subject.

[11] This subject has been reviewed by M. Hanack and H.-J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **6**, 666 (1967).

[12] Compare A. S. Kende and P. T. MacGregor, *J. Amer. Chem. Soc.*, **86**, 2088 (1964); L. Lombardo and D. Wege, *Tetrahedron Lett.*, 4859 (1972).

low, the favored[13,14] tricyclic cation **20b** can undergo exothermic conversion to **7** instead. The facile **6**-OAc → **7** transformation is also very likely associated with the intervention of **20b**.[13]

(13) (a) G. D. Sargent, N. Lowry, and S. D. Reich, *J. Amer. Chem. Soc.*, **89**, 5985 (1967); (b) L. A. Paquette and G. L. Thompson, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, paper ORGN 132; (c) L. A. Paquette and G. L. Thompson, *J. Amer. Chem. Soc.*, **95**, 2364 (1973).

(14) R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970); H. Gunther, *ibid.*, 5173 (1970).

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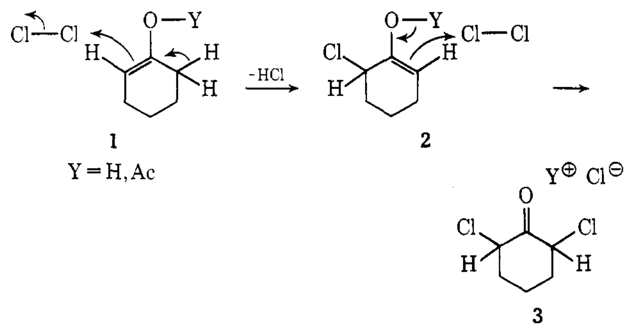
Origin of Disubstitution Products in Ketone Halogenation. A New Mechanism[1]

Sir:

Since the early studies of ketone halogenation,[2] the accepted mechanism for the acid-catalyzed reaction has been a rate-determining enolization followed by a rapid reaction of the enol with halogen to generate an α-halo ketone. However, the monosubstituted product is often accompanied by varying amounts of disubstituted product even in the presence of an excess of the ketone. During a study of the stereochemistry of ketone halogenation we have found that the disubstitution product is *not necessarily* formed by further reaction of the monosubstituted ketone as implied by the accepted mechanism, but instead may arise by a different pathway. We would like to report evidence that α,α'-disubstitution can occur by a mechanism with the basic features depicted in Scheme I.

Scheme I



The chlorination of 4-*tert*-butylcyclohexanone (**4**) in CCl_4 solution at 0–5° gave *cis,trans*-2,6-dichloro ketone **7** (19–30% of the chlorinated product), mp 41–42°[3] (but no *cis,cis*-2,6-dichloro ketone **8** by comparison with an authentic specimen, mp 148–150°[4]), inaddition to the mixture of *cis*- and *trans*-2-chloro ketones **5** and **6**.[5] Any 2,2-dichloro ketone **9** present was less than 0.6% of the dichloro portion of the product as determined by glpc comparison[5] with authentic **9**, mp 38.5–40°.[4] Attempts to minimize the formation of dichloro ketone by increasing the ketone:chlorine ratio produced some change (Table I), but the *ca.* twofold decrease in the dichloro:monochloro ketone ratio for a tenfold increase in ketone:chlorine ratio is not compatible with the dichloro ketone being formed from monochloro ketone by either an ionic or a radical mechanism. For an ionic mechanism this is even more evident when the $\sim 10^3$ weaker basicity[6] of the carbonyl oxygen in the monochloro ketone and its consequent slower rate of *acid*-catalyzed enolization[7] are taken into account. Conclusive evidence on the point came from control experiments in which pure *cis*- and pure *trans*-2-chloro-4-*tert*-butylcyclohexanone (**5** and **6**) were each treated with Cl_2–HCl–CCl_4 under the chlorination conditions. No dichloro ketone was produced nor was there any epimerization of the monochloro ketones, even with a larger amount of HCl present than would have been formed during chlorination of **4**. At 30° chlorination of **5** and **6** occurred slowly to produce a mixture of 2,6- *and* 2,2-dichloro ketones ($\sim$50% *cis, trans*-2,6 and $\sim$50% 2,2) each of which was stable under the reaction conditions. Light-catalyzed (>350 nm) radical chlorinations of both the *cis*- and *trans*-2-chloro ketones **5** and **6** in CCl_4 at −15° introduced chlorine at other points in the carbon skeleton but gave no 2,6-dichloro ketone **7**.

Table I. Chlorination of 4-*tert*-Butylcyclohexanone[a]

Concn of ketone in CCl_4, *M*	Molar ratio ketone:Cl_2	Monochloro:dichloro[b]
0.14	1	2.2–2.4
0.20	2	2.1
0.25	4	2.2
0.24	5	2.7
0.28	10	4.1

[a] Reactions conducted at 0–5°. [b] Determined by integration of the nmr peaks due to CHCl protons.

Since chlorination of 4-*tert*-butylcyclohexanone produces **7** under conditions not yielding this compound from either monochloro ketone **5** or **6** by ionic or radical paths and since ionic chlorination of either **5** or **6** at only 25° higher temperature produces not only **7** but an equal amount of the 2,2-dichloro ketone **9**, the 2,6-dichloro ketone from the reaction with 4-*tert*-butylcyclohexanone must arise without the intervention of monochloro ketone itself. The most reasonable alternative is the chloroenol path **1** → **2** → **3** (Y = H) in which the step **1** → **2** is concerted.[8] For

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(1) α-Halo Ketones. VII. For paper VI, see E. W. Warnhoff, C. M. Wong, and W. T. Tai, *J. Amer. Chem. Soc.*, **90**, 514 (1968).

(2) (a) A. Lapworth, *J. Chem. Soc.*, **85**, 30 (1904); (b) E. D. Hughes, H. B. Watson and E. D. Yates, *J. Chem. Soc.*, 3318 (1931); (c) H. B. Watson, *Chem. Rev.*, 7, 173 (1930); (d) C. K. Ingold and C. L. Wilson, *J. Chem. Soc.*, 773 (1934).

(3) The melting point and spectroscopic data are in agreement with those reported by F. Caujolle, J. Cantacuzene, and D. Q. Quan, *C. R. Acad. Sci., Ser. C*, 765 (1967).

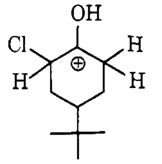
(4) The melting point and spectroscopic data are in agreement with those reported by J. Petrissans, S. Gromb, and J. Deschamps, *Bull. Soc. Chim. Fr.*, 4381 (1967).

(5) Quantitative analyses of the mixtures of the possible products **5**, **6**, **7**, **8**, and **9** were carried out by a combination of integration of the δ 3.5–5.5 region of 100-MHz nmr spectra of benzene and deuteriochloroform solutions and glpc at 120° with a 2-m column of 1% XE-60 on Gas-Chrom Q.

(6) G. C. Levy, *J. Amer. Chem. Soc.*, **92**, 6238 (1970).

(7) C. Rappe, *Acta Chem. Scand.*, **19**, 276 (1965).

(8) The carbonium ion i cannot be an intermediate on the way from



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