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]

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[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).

Leo A. Paquette,* Kay A. Henzel
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

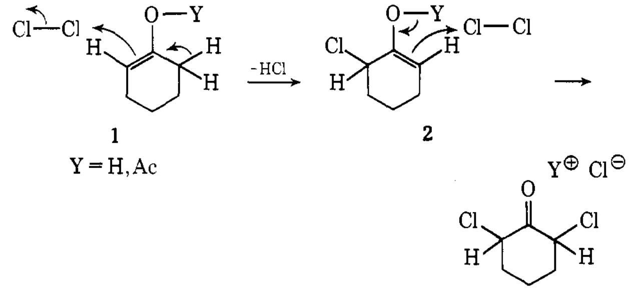
Received December 4, 1972

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



1
Y = H, Ac

2

3

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]), in addition 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 ~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 (~50% *cis, trans*-2,6 and ~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).

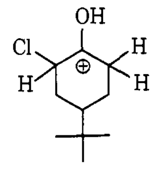
[4] The melting point and spectroscopic data are in agreement with those reported by J. Petrissans, S. Gromb, and J. Deschamps, *Bull. Soc. Chim. Fr.*, 4381 (1967).

[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).

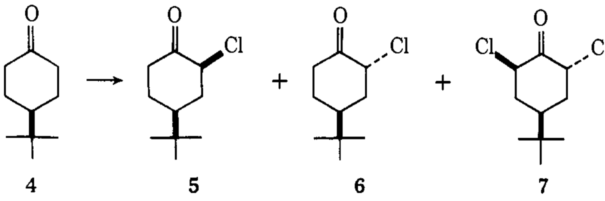
[8] The carbonium ion i cannot be an intermediate on the way from

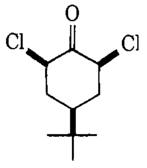


i

reaction **1** → **2** to be concerted would require favorable orientation of the available incipient chloride base at the α′-H instead of nearer the hydroxyl hydrogen, perhaps as in **10** which has analogy in the reaction of singlet oxygen with allylic systems,[9] except that the LUMO of chlorine is σ_u^* whereas the LUMO of singlet oxygen is π_g^*.

Support for such a mechanism was provided by the isolation of a chloroenol derivative when Y = Ac (Scheme I). Chlorination of the enol acetate of **4** in carbon tetrachloride at 5° gave, in addition to monochloro ketones **5** and **6**, as much as 30% of *trans*-6-chloro-1-acetoxy-4-*tert*-butylcyclohexene (**11**).[10] Treatment of **5** and **6** with AcCl–HCl–CCl$_4$ at 5° gave no **11**.





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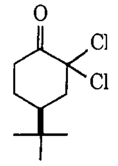
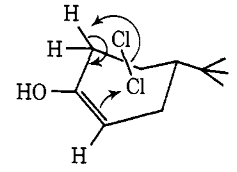
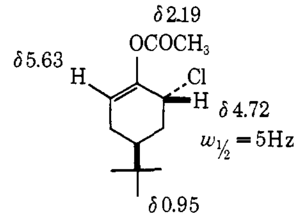


9



10



11

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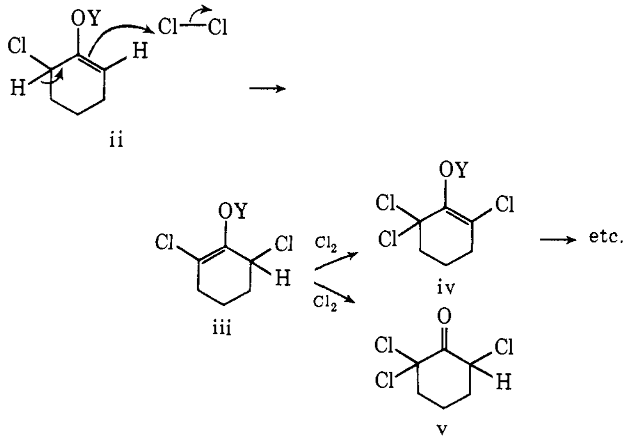
1 to 2; i would deprotonate from oxygen instead since **5** and **6** do not in fact enolize in the presence of HCl–Cl$_2$–CCl$_4$ under the conditions used although their carbonyl oxygens are protonated to some extent in this medium.

(9) C. S. Foote, *Accounts Chem. Res.*, 1, 104 (1968).

(10) The survival of **11** in the presence of some chlorine must be a consequence of the decreased nucleophilic character of the enolic double bond caused by the combined effect of the acetyl and allylic chlorine groups. Similarly, the absence of a continuation of reaction path 1 → 2 → 3 such as ii → iii → iv + v can be due to the greatly decreased reactivity of the dichloro enol iii with electrophiles.



The unexpected implication of the mechanism in Scheme I is that, at least in a nonpolar aprotic solvent in which proton removal from the enolic OH during halogenation is not facilitated by the solvent, electrophilic attack on an enol or its derivative with cleavage of an α′-CH bond to yield the α′-enol derivative **2** can be closely competitive with cleavage of the OY bond of **1** to form the monosubstituted ketone. It remains to be seen how general the α′-CH cleavage is.

K. E. Teo, E. W. Warnhoff*
Department of Chemistry, University of Western Ontario
London, Canada

Received January 5, 1973

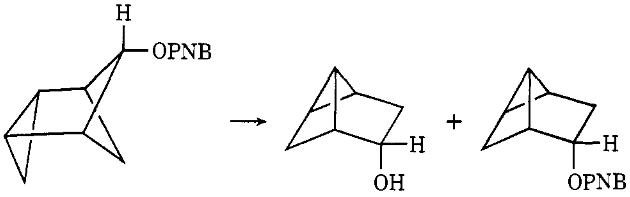
Solvolysis of Derivatives of *exo*- and *endo-anti*-Tricyclo[3.1.1.0^{2,4}]heptan-6-ol[1]

Sir:

The recent report by Masamune and coworkers,[2] on the solvolytic behavior of *exo-anti*-tricyclo[3.1.1.0^{2,4}]hept-6-yl *p*-nitrobenzoate (**1**), prompts us to disclose our related studies of **1** and of the epimeric *p*-nitrobenzoate (**2**) and *p*-toluenesulfonate (**3**) of *endo-anti*-tricyclo[3.1.1.0^{2,4}]heptan-6-ol (**4**).

The synthesis of the alcohol precursors of **1**, **2**, and **3** has been previously discussed.[3] In a series of 13 steps starting from the known[4] *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene, we were able to prepare an 86:14 mixture of **4**:**5** in 4.5% over-all yield. The conversion of **5** into **1** and of **4** into **2** and **3** was readily accomplished.

The solvolysis of **1** gave 61% of **6** and 22% of **7** (*via* internal return). The structure of **6** was based on spectral comparison with an authentic sample.[5] Lithium aluminum hydride reduction of **7** gave **6**. The acetolysis of **3** gave 52% of **8**, 35% of **9**, and 11% of **10** after conversion of the acetates to the corresponding alcohols *via* hydride reduction. The identification of **8** was based on comparison with an authentic sample, while the structural assignment for **9** was made on the basis of spectral evidence and its facile dehydration to **8**. The spectral properties of **10** were consistent with the assigned structure. Furthermore, catalytic reduction of **10** gave *exo*-2-hydroxybicyclo[4.1.0]heptane (**11**) which was identical with an authentic sample.[6]



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(1) Paper XXXVII on The Chemistry of Bent Bonds. For the previous paper in the series, see P. Gassman and W. J. Greenlee, *J. Amer. Chem. Soc.*, 95, 980 (1973).

(2) S. Masamune, R. Vukov, M. J. Bennett, and J. T. Purdham, *J. Amer. Chem. Soc.*, 94, 8239 (1972).

(3) For the initial report of the synthesis of the tricyclo[3.1.1.0^{2,4}]heptyl ring system see: P. G. Gassman and X. Creary, 163rd National Meeting of the American Chemical Society, Boston, Mass., April 9–14, 1972, Abstracts, ORGN 140.

(4) H. E. Simmons and R. D. Smith, *J. Amer. Chem. Soc.*, 81, 4256 (1959).

(5) R. K. Lustgarten, *J. Amer. Chem. Soc.*, 94, 7602 (1972). We wish to thank Professor Lustgarten for providing the spectra of authentic **6**.

(6) P. G. Gassman and T. J. Atkins, *J. Amer. Chem. Soc.*, 94, 7748 (1972).