Tricyclo[2.2.0.0²,⁶]hexane

BY DAVID M. LEMAL AND KYUNG S. SHIM

The highly strained title hydrocarbon was prepared by mercury-sensitized photolysis of nortricyclanone. Coupled with microanalytical and spectral data, hydrogenation studies established the correctness of the structure assignment. Anomalous features of the hydrogenolysis of this substance emphasize the influence of angle strain on chemical properties.

Because the properties of highly strained molecules afford insight into the nature of chemical bonding, the synthesis of small polycyclic systems has arrested our interest. We wish to report that mercury-sensitized photolysis of nortricyclanone (2)[1] affords the title hydrocarbon 1 in yields up to 5%. This substance is the first parent tricyclohexane, though Meinwald and his co-workers have recently reported derivatives (3 and 4) of this and another tricyclohexane.[3]

1 **2**

3 **4**
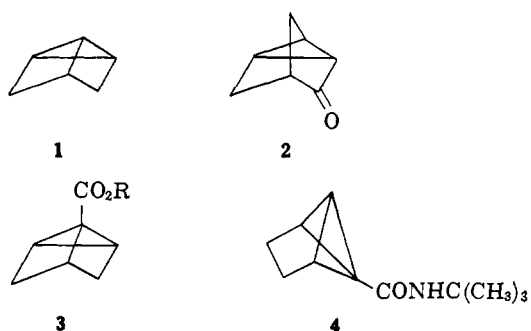
Nortricyclanone was prepared in 35–40% over-all yield from norbornene (two steps)[4] or from norbornadiene (three).[5] Ultraviolet irradiation of a mixture of ketone and mercury vapor produced carbon monoxide, hydrogen, benzene, an impressive quantity of polymer, and a volatile liquid subsequently identified as 1. Vacuum transfer of the volatile photolysis product (plus remaining nortricyclanone) followed by vapor chromatography made the unknown compound available in pure form. This liquid, which had a shorter retention time than benzene on Ucon Polar, displayed ultraviolet end absorption of such low intensity that the molecule clearly lacked unsaturation. Absence in the n.m.r. spectrum of absorption below ~7 τ provided support for this conclusion. A prominent infrared band at 3.27 μ betokened the presence of carbon–hydrogen bonds with a high degree of s-character, as expected for a very strained ring system.[3b,6] Microanalytical results fit the empirical formula C_6H_8, and measurement of the mass spectrum of the unknown hydrocarbon at low ionization potentials confirmed the molecular weight of 80. These data served to establish that the compound was a tricyclohexane, but hydrogenation studies were required before a rigorous decision could be made among the several sterically feasible isomers.

(1) Srinivasan (ref. 2) has demonstrated some of the synthetic potentialties of mercury-sensitized photodecomposition of saturated ketones.

(2) R. Srinivasan, J. Am. Chem. Soc., 83, 4923 (1961).

(3) (a) J. Meinwald. Abstracts of the 18th Annual Organic Chemistry Symposium of the American Chemical Society, Columbus, Ohio, 1963, pp. 43, 44; (b) J. Meinwald, C. Swithenbank, and A. Lewis, J. Am. Chem. Soc., 85, 1880 (1963).

(4) D. M. Lemal and A. J. Fry, J. Org. Chem., in press.

(5) H. K. Hall, Jr., J. Am. Chem. Soc., 82, 1209 (1960).

(6) G. L. Closs and L. E. Closs, ibid., 85, 2022 (1963).

Absorption of nearly 2 moles of hydrogen over 30% palladium–charcoal in β-ethoxyethanol proceeded rapidly at room temperature. Vapor chromatography of the product revealed two compounds in a ratio of approximately 20:1. The major component was identified as methylcyclopentane by comparison with an authentic sample in terms of g.l.c. (gas–liquid chromatographic) retention times and infrared spectra. When the hydrogenation was conducted in diglyme with 10% palladium–charcoal, the rate of consumption was still fast but the ratio of methylcyclopentane to its congener after uptake had ceased was only 77:23.[7] Assuming that the minor product resulted from the absorption of only a single mole of hydrogen, the consumption calculated from this ratio was 1.77 moles; the observed was 1.73.

It was useful to make the mechanistically sound (vide infra) guess that structure 1 was the correct representation of the unknown tricyclohexane. Hydrogenolysis of a single carbon–carbon bond of 1 could lead to any of five hydrocarbons, depending upon which of the five types of bond were cleaved. Rupture of bonds a through e would yield hydrocarbons 5 through 9, respectively. Comparison of the g.l.c. retention time (on Ucon Polar) of the unknown hy-

1 **5** **6**

7 **8** **9**
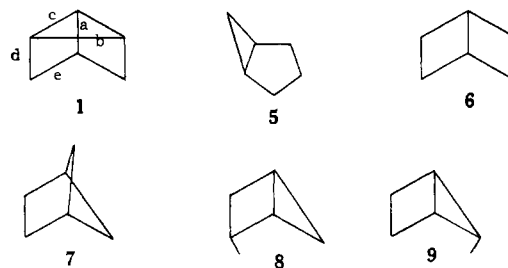
drogenation product with the times for authentic samples of 5 and 6 eliminated these compounds from consideration, but the retention time of authentic bicyclo[2.1.1]hexane (7) was identical with that of the unknown. Moreover, the n.m.r. spectra of 7 and the unknown were indistinguishable.

Aside from 1, the only tricyclohexane which could reasonably lead to 7 when hydrogenated is the bridged bicyclobutane 10. The unknown hydrocarbon 10 contains only three different sets of equivalent protons, and these sets are expected to be coupled only weakly as judged from the simple n.m.r. spectrum of the carboxamide derivative 4.[3] Hence interpretation of the n.m.r. spectrum of 10 should be straightforward. In contrast, structure 1 contains five different kinds of protons, and the molecular geometry is such that strong spin

(7) The authors wish to thank Prof. J. A. Berson for suggesting the use of an ether solvent to minimize the twofold hydrogenolysis to methylcyclopentane.
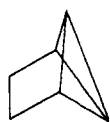
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coupling should exist between nonequivalent sets. A complex pattern of lines is to be anticipated; the experimental spectrum offers no disappointment. A group of multiplets is found in the 7–7.8 τ and another multiplet in the 8.2–8.5 τ region. The absorption intensity in the two regions is approximately equal. Spectral, microanalytical, and hydrogenation data have thus established the structure **1** for the photolysis product of nortricyclanone.

When the hydrogenation of **1** in diglyme over 10% palladium–charcoal is interrupted after absorption of only about 1 mole, the product displays g.l.c. peaks characteristic of starting material, methylcyclopentane, bicyclo[2.1.1]hexane, and a fourth compound which is transformed into methylcyclopentane by prolonging the hydrogenation. The unknown substance, which comprises about one-fourth of the total mixture, was identified as 1-methylcyclopentene by gas–liquid chromatographic analysis and by infrared and n.m.r. spectral comparison with authentic material. Formation of the olefin from **1** corresponds to addition of 1 mole of hydrogen and rearrangement. Use of strontium carbonate as catalyst support gave results similar to those with charcoal, so the possibility of acid catalysis could be discounted. Since 10% palladium-on-charcoal alone had no effect upon the tricyclohexane **1**, it was clear that addition of hydrogen preceded rearrangement. Potential hydrogenolysis product **5** was shown, like **7**, to be inert under the hydrogenation conditions. Strained bicyclic hydrocarbon **9** (or perhaps **8**) may well be an intermediate on the pathway to 1-methylcyclopentene, but the possibility remains that rearrangement follows net addition to **1** of only one, not two hydrogen atoms.

Whichever may be the case, it is difficult to avoid the conclusion that the initial step toward olefin is cleavage of a four-membered ring despite the gentleness of the reaction conditions. 1-Methylcyclopentene accumulates considerably faster than bicyclo[2.1.1]hexane even though the olefin is subject to further hydrogenation. Hence scission of a four-ring of **1** is apparently much more rapid than that of the three. In the absence of an activating functional group such an event is without precedent, and its occurrence here underlines the high degree of angle strain incorporated into the tricyclo[2.2.0.0^{2,6}]hexane molecule.[8]
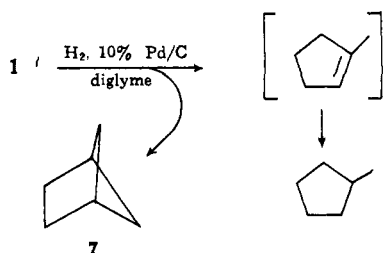
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Returning once again to the photolysis step, considerable experimentation was devoted to optimizing the conditions for this reaction. Not surprisingly, irradiation of **2** with an unfiltered Hanovia 450-watt Type L mercury arc in saturated hydrocarbon solvents gave alcohols, ethers, and carbonyl compounds arising from attack upon the solvent after photoexcitation, and the C-6 fraction of the product was negligible.[9] Vapor phase photolysis at 80° in the absence of a sensitizer yielded primarily polymeric material accompanied by extremely small amounts of benzene and of **1**. Irradiation in Vycor of ketone vapor in the presence of mercury vapor led to yields of **1** ranging as high as 5%, and benzene yields were comparable.[10] At 80° the vapor pressure of nortricyclanone is approximately 25 mm.; increasing the total pressure by addition of variable quantities of nitrogen failed to improve yields in either the sensitized or unsensitized photolyses. Possible reasons for the low yields will be considered below.

The light source which was used in the sensitized photolyses is a circular array of low-wattage lamps which emit a relatively large fraction of their total output at 2537 Å.[2] Since mercury vapor is quite opaque to this frequency and since saturated ketones have very low extinction coefficients in the near ultraviolet, the primary energy source for the ketone is the 6^3P_1 state of the metal, 112 kcal./mole above the ground state.[11] Excited by collision with "hot" mercury atoms, nortricyclanone decomposes largely by loss of carbon monoxide,[12] generating the biradical **11** or its equivalent. Coupling of **11** yields the tricyclohexane **1** (*cf.* the analogous transformation of cyclopentanone into cyclobutane,[13] for example, and **13** into **7**[2]). A likely alternative fate for the biradical provides an explanation for benzene formation. Rearrangement of the cyclopropyl radical of **11** to an allylic radical[14] followed by shift of a hydrogen would give the cyclohexadienes **12**. The dienes would possess a great excess of internal energy, perhaps sufficient to bring about fragmentation into benzene and hydrogen (major products of pyrolysis of **12**[15]). Even if the dienes escaped decomposition at this stage, benzene and hydrogen would very probably be produced *via* subsequent excitation by "hot" mercury atoms.[16] In any event, mass spectra of the uncondensable gas from the sensitized photodecompositions revealed substantial amounts of hydrogen in addition to carbon monoxide.

Another possible mode of decomposition for the biradical **11** deserves mention. When 1,4-biradicals (or

(8) Meinwald (ref. 3a) has noted that **3** yields carboalkoxymethylcyclopentane when hydrogenated, a result consistent only with cleavage of the three- in preference to one of the four-membered rings.

(9) See, for example, P. de Mayo in "Advances in Organic Chemistry, Methods and Results," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1960, p. 367.

(10) Yields are based on ~70% conversion.

(11) W. A. Noyes and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Corp., New York, N. Y., 1941, Chaper V.

(12) Manometric measurements during photolysis indicated that a substantial fraction of the ketone was destroyed by pathways not involving the loss of carbon monoxide. The relatively great strength of the cyclopropyl-to-carbonyl bond (ref. 14) may be responsible in some measure for this result [*cf.* the low quantum yield for carbon monoxide formation in the direct photolysis of methyl cyclopropyl ketone: J. N. Pitts and I. Norman, *J. Am. Chem. Soc.*, **76**, 4815 (1954)].

(13) R. Srinivasan, *ibid.*, **83**, 4344 (1961).

(14) For a discussion of the conditions for formation and rearrangement of cyclopropyl radicals see D. I. Schuster and J. D. Roberts, *J. Org. Chem.*, **27**, 51 (1962).

(15) F. O. Rice and A. L. Stallbaumer, *J. Am. Chem. Soc.*, **64**, 1527 (1942).

(16) R. Srinivasan, *ibid.*, **84**, 3982 (1962).
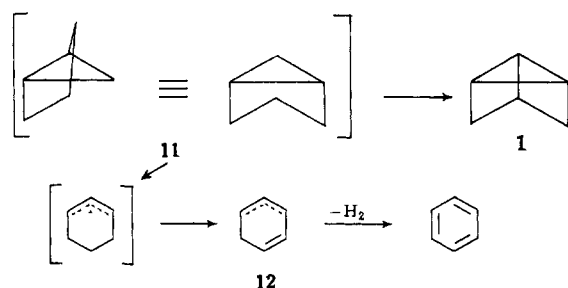
their equivalent) are produced by any of a variety of reaction types, cleavage of the central bond is a commonly observed consequence.[17] This is illustrated by formation of 1,5-hexadiene (14) in the mercury-sensitized photolysis of norcamphor (13) studied by Srinivasan.[2] The corresponding transformation for nortricyclanone would lead to 3-allylcyclopropene (15), which should polymerize with very little provocation. Hence production of 15 may account in part for the low yields of volatile products in the photolysis of 2. Moreover,
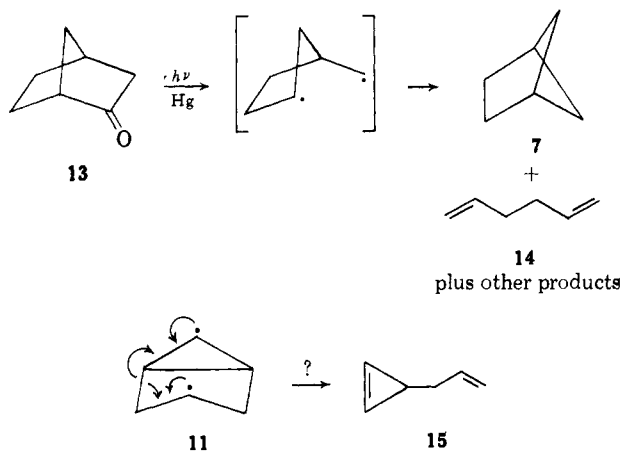
the relatively high reactivity of the tricyclic hydrocarbon 1 (as judged by the vigor with which it absorbs hydrogen) makes it particularly vulnerable to attack by radicals or by "hot" mercury atoms during the photolysis. We have recently designed a flow system which should minimize losses from this source by removing 1 from the reaction vessel as it is formed.[18]

Aspects of the chemistry of tricyclo[2.2.0.0^{2,6}]hexane are currently under investigation in our laboratory. It is now possible to obtain 1 in yields as high as 36% (at 30% conversion) by photolysis of nortricyclanone using a "quasi-flow" technique. The reaction vessel is attached through a liquid nitrogen trap and a manostat to a mechanical pump, and the system is maintained at 100 mm. Tricyclo[2.2.0.0^{2,6}]hexane collects in the trap as the photolysis progresses. Decomposition of this hydrocarbon by "hot" mercury atoms was probably the major source of benzene in earlier experiments because photolysis by the present technique affords practically no benzene (or cyclohexadienes).

Experimental[19]

Materials.—Nortricyclanone (2) synthesized according to the method of Hall[5] was purified by g.l.c. at 130° on the preparative

column. Methylcyclopentane (Aldrich Chemical Co.) was similarly purified using the analytical column. Bicyclo[2.1.1]-hexane (7) was prepared by mercury-sensitized photolysis of norcamphor[2] (Aldrich Chemical Co.) and was separated from the complex volatile fraction of the reaction mixture by g.l.c. at 40° on the analytical column. The n.m.r. spectrum was identical with that given in the literature. Bicyclo[2.2.0]hexane, prepared by the same reaction, was kindly provided by Dr. Kenneth Kirk. The Simmons-Smith reaction was used for the preparation of bicyclo[3.1.0]hexane.[20] Comparison of the boiling point and refractive index with the literature values[21] confirmed the identity of this compound, which was further purified by vapor chromatography on the analytical column.

Procedure.—The light source used for the mercury-sensitized photolyses has been described by Srinivasan.[2] Nortricyclanone (4 g., 0.037 mole) and mercury (5 g.) were introduced into a 2-l. Vycor flask fitted with a three-way stopcock connected to a vacuum pump and inlet for prepurified nitrogen. The mixture was covered with glass wool to prevent direct irradiation of the liquid phase. When the flask had been alternately evacuated and refilled with nitrogen several times, it was cooled to −78°, evacuated to 0.1 mm., and sealed. The bottom of the flask was warmed to and maintained at ∼80° with a heating mantle; the upper parts were kept slightly warmer with a sunlamp to prevent condensation of ketone or mercury on the walls. After a 24-hr. irradiation period the photolysis was stopped. The flask was cooled to room temperature and a portion of the gaseous products was removed. Hydrogen was shown to be present mass spectrometrically. Carbon monoxide was detected by comparison of its vapor chromatographic retention time with that of an authentic sample on a 6-ft. activated silica gel column.

The volatile liquid products were removed by vacuum transfer to a trap cooled by liquid nitrogen. This mixture was then separated on the preparative column into unreacted ketone and a much more volatile fraction. Vapor chromatography of the latter on the analytical column at 43° revealed only two major peaks, later shown to correspond to tricyclo[2.2.0.0^{2,6}]hexane (1) and benzene (in order of retention time). The yields of the two hydrocarbons in one experiment were 4.6 and 2.8%, respectively, based on the recovery of 27.5% of unreacted nortricyclanone. These figures varied somewhat from run to run. Benzene was identified by its n.m.r. spectrum and by its g.l.c. retention time.

The tricyclohexane displayed prominent infrared absorption maxima in carbon tetrachloride at 3.27 (s), 3.33 (s), 3.40 (s), 3.49 (s), 7.79 (m), 8.06 (s), 8.79 (s), 8.96 (m), 9.67 (m), 10.45 (m), 10.83 (m), 11.59 (s), and 14.16 μ (m). Its n.m.r. spectrum is presented in the Discussion. The molecular weight was determined by measurement of the mass spectrum at several ionization voltages in the range 10–17.5 v. At most of these values the parent peak (m/e 80) is the base peak, but the p − 1 becomes the base peak at the upper end of the range.

Anal. Calcd. for C$_6$H$_8$: C, 89.94; H, 10.06. Found: C, 89.94; H, 10.00.

Small-scale hydrogenations of the tricyclo[2.2.0.0^{2,6}]hexane were carried out in a conventional atmospheric pressure hydrogenation apparatus, but the sample was introduced in a special manner. A sealed ampoule fashioned with a hook at one end and containing a weighed quantity of hydrocarbon was suspended from a horizontal glass hook mounted above the solvent–catalyst mixture (as in many microhydrogenation setups). Being attached to a ground joint, the latter hook could be rotated so as to drop the ampoule into the solvent where it would be crushed by the magnetic stirring bar. This technique has the advantage that losses due to volatilization of low-boiling samples during flushing and equilibration of the system are completely eliminated.

In a typical run, a mixture of 1.5 ml. of diglyme (freshly distilled from lithium aluminum hydride) and 45 mg. of 10% palladium-on-charcoal was allowed to equilibrate under an atmosphere of hydrogen; 90 mg. of the tricyclohexane 1 was introduced as described above and the system was quickly rezeroed when the ampoule was broken. Hydrogen consumption ceased after 35

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(17) For fragmentation reactions of this type involving cyclic azo compounds, for example, see C. G. Overberger, G. Kesslin, and N. R. Byrd, J. Org. Chem., 27, 1568 (1962); S. G. Cohen, S. Hsiao, E. Saklad, and C. H. Wang, J. Am. Chem. Soc., 79, 4400 (1957).

(18) Srinivasan (ref. 2) noted that yields of 7 from 13 were much lower at high than at low conversions, and proposed the use of a flow system to remedy the situation.

(19) Except where specified otherwise, vapor chromatograms were run on either of two columns, designated as preparative (1 in. × 8.25 ft. packed with 20% w./w. Ucon Polar on acid-washed Chromosorb P, 30/60 mesh) and analytical (0.25 in. × 6.5 ft. packed with 20% w./w. Ucon Polar on acid-washed Chromosorb W, 30/60 mesh). N.m.r. spectra were measured at 60 Mc./sec. on a Varian A-60 spectrometer using carbon tetrachloride as solvent and tetramethylsilane as internal standard.

(20) R. S. Shank and H. Shechter, J. Org. Chem., 24, 1825 (1959).

(21) H. E. Simmons and R. D. Smith, J. Am. Chem. Soc., 81, 4256 (1959).

min., during which 48.0 ml. (23°, 744.2 mm.) had been absorbed. The catalyst was removed by suction filtration at about −80°. Vapor chromatography of a sample of the filtrate on the analytical column revealed in addition to solvent two peaks of relative area 77:23. These volatile products were transferred *in vacuo* at room temperature into a liquid nitrogen trap to separate them from the high-boiling diglyme. The mixture was once again subjected to g.l.c. and the two peaks were trapped separately. Comparison of the g.l.c. retention time and infrared spectrum with those of an authentic sample identified the larger peak as methylcyclopentane. Identity with authentic material in terms of retention times and n.m.r. spectra established that the peak of smaller area was bicyclo[2.1.1]hexane (7). The hydrogen uptake required to produce a 77:23 mixture of methylcyclopentane and 7 is calculated to be 1.77 equivalents; the observed 48.0 ml. uptake corresponds to 1.73 equivalents, or about 2% less than the theoretical.

Another hydrogenation experiment using the same solvent and catalyst was arbitrarily interrupted after only about 0.9 equivalent of hydrogen had been absorbed. A vapor phase chromatogram of the volatile products displayed peaks (in order of increasing retention time) corresponding to methylcyclopentane, bicyclo[2.1.1]hexane, unidentified product, and starting material. Relative areas were 25:13:24:38. Further hydrogenation of this mixture resulted in the disappearance of the unidentified peak as well as starting material, and again only methylcyclopentane and 7 remained. The unknown substance was tentatively identified as 1-methylcyclopentene by its n.m.r. spectrum. An authentic, chromatographically homogeneous sample of this compound

was prepared by dehydration with 85% phosphoric acid of 1-methylcyclopentanol. Comparison (retention times; infrared, n.m.r. spectra) with the unknown confirmed the structure assignment. It is important to note that the n.m.r. spectrum of the crude hydrogenation product had revealed the presence of 1-methylcyclopentene, thus ruling out the possibility that the olefin was an artifact arising from g.l.c.

Six per cent palladium–strontium carbonate was substituted for the 10% palladium–charcoal used in the preceding hydrogenation experiment in order to eliminate acid catalysis as an explanation for olefin formation. The product distribution corresponded closely with that observed using charcoal as the support. When a diglyme solution of 1 was stirred with 10% palladium–charcoal for many hours in the absence of hydrogen, the tricyclic compound remained unchanged as indicated by g.l.c.

The bicyclic hydrocarbon 5 failed to absorb hydrogen at atmospheric pressure over 10% palladium–charcoal in diglyme solution. Vapor chromatography of the product revealed only starting material.

[Contribution from the Avery Laboratory, University of Nebraska, Lincoln, Neb.]

Elimination Reactions of α-Halogenated Ketones. XII.[1a] Carbon–Halogen and Carbon–Hydrogen Bond Strengths as Orientation and Rate-Determining Factors. Deuterium Isotope Effects in Dehydrobromination of 2-Bromo-2-benzyl-1-indanone[1b]

By Dennis N. Kevill, Guillaume A. Coppens, and Norman H. Cromwell[1c]

It has been found that, in halide ion promoted elimination from α-halogenated tetralones and indanones, the strength of the carbon–halogen bond is an extremely important rate-determining factor. Deuterium substitution for the *exo*-benzylic methylene protons of 2-bromo-2-benzyl-1-indanone (IV) leads to a low deuterium isotope effect, consistent with the transition state of the rate-determining step having carbon–halogen bond breaking running well ahead of carbon–hydrogen bond breaking. Attack of piperidine upon 2-bromo-2-(α,α-dideuteriobenzyl)-1-indanone (IVa) leads to substantial yields of 3-piperidino-2-(α,α-dideuteriobenzyl)-1-indanone (VIa) formed by an endocyclic dehydrobromination followed by a 1,4-addition. The exocyclic deuterium substitution leads to a marked change in the reaction pathway and suggests the possible use of deuterium substitution for controlling the orientation of elimination in other delicately balanced systems.

Previous communications within this series have reported upon the kinetics of elimination reactions of several α-halogenated tetralones[1–6] and of 4-biphenylyl 1-bromocyclohexyl ketone.[7] These reactions were discussed in terms of a mechanism of merged substitution and elimination.[3,8]

More recently it was proposed elsewhere[9] that bimolecular dehydrohalogenation from tertiary halide

structures proceeds by a mechanism similar to the classical E2 mechanism but with the reaction passing through a transition state in which a considerable amount of E1 character is incorporated. These two mechanisms differ only subtly in character.[6] Both incorporate considerable carbon–halogen bond breaking in the transition state accompanied by only a weakly developed rupture of the carbon–hydrogen bond. This present communication reports upon studies which show that bimolecular dehydrohalogenation of tertiary α-halogenated ketones can proceed *via* a transition state which incorporates both of these features.

Discussion of Results

Halide ion promoted elimination from 2-benzyl-2-halogeno-4,4-dimethyl-1-tetralone in acetonitrile was found to lead exclusively to the thermodynamically

(1) (a) For paper XI in this series see D. N. Kevill, P. W. Foster, and N. H. Cromwell, *J. Org. Chem.*, **28**, 1476 (1963). (b) Presented in part at the XIXth International Congress of Pure and Applied Chemistry, London, July 10–17, 1963. (c) To whom communications concerning this article should be addressed.

(2) D. N. Kevill and N. H. Cromwell, *J. Am. Chem. Soc.*, **83**, 3812 (1961).

(3) D. N. Kevill and N. H. Cromwell, *ibid.*, **83**, 3815 (1961).

(4) G. A. Coppens, D. N. Kevill, and N. H. Cromwell, *J. Org. Chem.*, **27**, 3299 (1962).

(5) D. N. Kevill, G. A. Coppens, and N. H. Cromwell, *ibid.*, **28**, 567 (1963).

(6) D. N. Kevill and N. H. Cromwell, *Tetrahedron Letters*, **4**, 255 (1963).

(7) D. N. Kevill, P. H. Hess, P. W. Foster, and N. H. Cromwell, *J. Am. Chem. Soc.*, **84**, 983 (1962).

(8) D. N. Kevill and N. H. Cromwell, *Proc. Chem. Soc.*, 252 (1961).

(9) (a) J. F. Bunnett, G. T. Davis, and H. Tanida, *J. Am. Chem. Soc.*, **84**, 1606 (1962). (b) Trends observed on extending measurements to other

than halide leaving groups have caused some amplification of the views expressed in ref. 9a: J. F. Bunnett and E. Baciocchi, *Proc. Chem. Soc.*, 238 (1963). It is interesting to observe that these trends are fully consistent with, and can be predicted from, the mechanism of merged substitution and elimination.[3,4]