

pure cyclohexanecarboxylic acid added to dilute the sample in the competitive rate runs. The deuterium analysis of the ester recovered from g.l.c. separation allowed computation of the mole fraction of deuterated species (m) in the sample: $m = (\text{atom } \% \text{ D})/7.14$, where 7.14 is taken as the maximum atom $\%$ D for the α -deuteriocyclohexanecarboxylic acid. The mole fraction of the undeuterated species is then $1 - m$ and

$$m \left(\frac{H_i + D_i}{2} \right) = D_f$$

$$(1 - m) \left(\frac{H_i + D_i}{2} \right) = H_f$$

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, INDIANA]

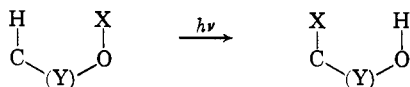
Mechanisms of Substitution at Unactivated Carbon Atoms¹

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Various mechanisms by which substitution at an unactivated carbon atom can occur have been defined. Most of the work has been carried out using the 1,3,3-trimethylcyclohexyl system, I, where X = Br, OH, p -OSO₂C₆H₄CH₃, and p -O₂CC₆H₄NO₂. The bicyclic ether II, 6-oxa-1,5-dimethyl[3.2.1]bicyclooctane, has been shown to be formed by: 1, a free-radical process (I, X = OH $\xrightarrow{Cu^+}$ II); 2, a radical-pair cage process (I, X = Br $\xrightarrow{h\nu}$ II); 3, a free cation process (I, X = Br $\xrightarrow{Ag^+}$ II); and 4, an ion-pair process (I, X = OSO₂C₆H₄CH₃ \rightarrow II).^{8,9} Of all reactions studied only the solvolysis of the p -nitroperbenzoate (I, X = O₂CC₆H₄NO₂) did not give rise to bicyclic ether II, furnishing instead keto alcohols V and VI *via* a Criegee rearrangement.¹³

With a few notable exceptions, organic chemists in the past have focused their attention on reactions which take place because of some form of chemical activation; reactions at unactivated carbon atoms have been largely ignored because of their presumed lack of specificity. It has become increasingly evident, however, that in molecules possessing favorable geometry reactions at unactivated atoms can become quite specific. Examples are the transannular reactions studied extensively by Cope³ and Prelog³ and the reaction which has come to be known as the Barton reaction in which an exchange of various groups, X, for hydrogen is photochemically induced.⁴



The Barton reaction has proved to be an extremely powerful tool in organic synthesis⁴ and as such is deserving of a detailed mechanistic study. In this paper we report the results of experiments undertaken both to determine the scope and limitations of the Barton reaction and related processes as well as to define the various mechanisms by which substitution at a saturated carbon atom can occur.

If one generalization emerges from our work it is that, contrary to the generally held notion that reactions at unactivated atoms are unselective, Barton-type reactions can and do become extremely selective and they take place by a myriad of mechanisms.

(1) Based on the Ph.D. Thesis of N. P. Matheny, Purdue University, 1964. Some of the work described in this paper has appeared in a preliminary communication: R. A. Sneen and N. P. Matheny, *J. Am. Chem. Soc.*, **86**, 3905 (1964).

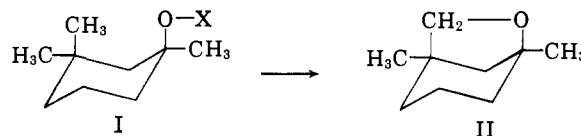
(2) David Ross Fellow, Purdue Research Foundation, 1963–1964.

(3) V. Prelog and J. G. Traynham in "Molecular Rearrangements," P. de Mayo, Ed., Part 1, Interscience Publishers, Inc., New York, N. Y., 1963, p. 593.

(4) O. L. Chapman in "Advances in Photochemistry," W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Eds., Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963, p. 399.

Results and Discussion

Most of our work has been carried out using the 1,3,3-trimethylcyclohexyl system,⁵ I, where X = Br, OH, p -OSO₂C₆H₄CH₃, and p -O₂CC₆H₄NO₂. The bicyclic ether, 6-oxa-1,5-dimethyl[3.2.1]bicyclooctane (II), has been shown to be formed by: 1, a free-radical process (I, X = OH $\xrightarrow{Cu^+}$ II); 2, a radical-pair cage process (I, X = Br $\xrightarrow{h\nu}$ II); 3, a free cation process (I, X = Br $\xrightarrow{Ag^+}$ II); and 4, an ion-pair process (I, X = OSO₂C₆H₄CH₃ \rightarrow II).⁸



Free-Radical Decomposition of Hydroperoxide (I, X = OH) to Bicyclic Ether II.—Cuprous chloride catalyzes the decomposition of 1,3,3-trimethylcyclohexyl hydroperoxide (I, X = OH) to bicyclic ether II. The only other apparent organic product is the parent alcohol I (X = H). That the reaction is free radical in nature is suggested by the studies of Kochi¹⁰ and Kharasch¹¹ and is confirmed by the results of studies of the decomposition in the presence of thiophenol, a good radical transfer agent. At low concentrations of added thiophenol (0.0033 *M*, equimolar with hydroperoxide)

(5) Data of Allinger⁶ and of Eliel⁷ suggest that 1,3,3-trimethylcyclohexanol (I, X = H) will exist preferentially (*ca.* 90%) in the conformation shown below with the hydroxyl group oriented in an axial position. A change in the nature of the group, X, would not be expected to affect this conformational preference greatly.

(6) N. L. Allinger and M. A. Miller, *J. Am. Chem. Soc.*, **83**, 2145 (1961).

(7) E. L. Eliel and H. Haubenstock, *J. Org. Chem.*, **26**, 3504 (1961).

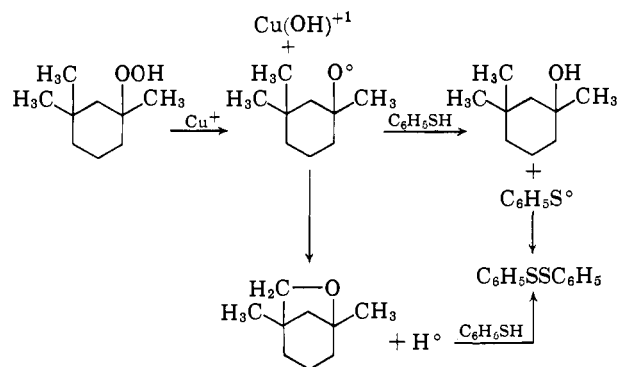
(8) This latter process had earlier been reported by Corey and White⁹ who used, however, the p -nitrobenzenepersulfonate.

(9) E. J. Corey and R. W. White, *J. Am. Chem. Soc.*, **80**, 6686 (1958).

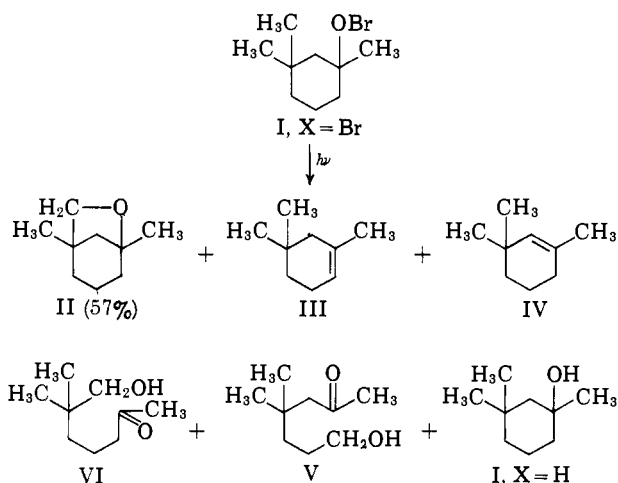
(10) J. K. Kochi, *ibid.*, **85**, 1958 (1963), and references cited therein.

(11) M. S. Kharasch, A. Fono, and W. S. Nudenberg, *J. Org. Chem.*, **16**, 113 (1951); M. S. Kharasch and A. Fono, *ibid.*, **24**, 606 (1959), and references cited therein.

diphenyl disulfide (analyzed by infrared spectroscopy) accompanied the bicyclic ether and alcohol as a product of the reaction. At higher concentrations of thiophenol (0.014 *M*) the formation of bicyclic ether was suppressed; only 1,3,3-trimethylcyclohexanol and diphenyl disulfide were formed. Apparently thiophenol functions at the higher concentration to trap the initially formed alkoxy radical, suppressing the competing radical insertion process, and diverting the alkoxy radical to alcohol.



Radical Cage Decomposition of Hypobromide (I, X = Br) to Bicyclic Ether II.—Light catalyzes the decomposition of 1,3,3-trimethylcyclohexyl hypobromite (I, X = Br) to give, ultimately, the bicyclic ether II (57% by vapor phase chromatography), accompanied by small amounts of 1,3,3-trimethylcyclohexanol (I, X = H), 1,5,5-trimethylcyclohexene (III), 1,3,3-trimethylcyclohexene (IV), 4,4-dimethylheptan-6-ol (V), and 2,2-dimethylheptan-6-ol (VI). Structure proofs for the olefins III and IV and keto alcohols V and VI are given in a subsequent section. Since



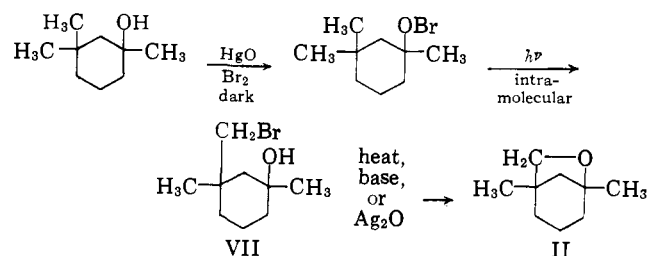
these four compounds and the alcohol are probably formed by straightforward mechanistic processes,¹² they will not be considered in detail here.

The light-induced formation of bicyclic ether II from hypobromite I (X = Br) is of considerable theoretical and practical interest. Our experiments have

(12) The alcohol I (X = H) is presumably formed by the action of hydrogen bromide on the hypobromite, and the alkenes III and IV are probably formed by the acid-catalyzed dehydration of this alcohol. Control experiments establish that these reactions do indeed occur. The keto alcohols would seem to be formed by a process, perhaps radical in nature, analogous to the rearrangement¹³ of 9-decalyl *p*-nitroperbenzoate, studied extensively by Criegee (*vide infra* under Ion-pair Decomposition of *p*-Nitroperbenzoate).

(13) P. A. S. Smith in ref. 3, p. 569.

established the following facts about this transformation: the hypobromite (formed *in situ* by the action of mercuric oxide and bromine on the alcohol I (X = H)) is a direct precursor, stable in the absence of light; it is photochemically converted by an intramolecular process¹⁴ to a second precursor, the rearranged bromohydrin,¹⁵ 1,3-dimethyl-3-bromomethylenecyclohexanol (VII), which in turn can be converted to bicyclic ether II, either thermally, or by the action of base, or by the action of silver oxide. Evidence for the details of this over-all transformation are given below.



The hypobromite I (X = Br) has not been isolated. It was prepared *in situ* and in the absence of light by the action of bromine and mercuric oxide on a pentane solution of the alcohol. The ultraviolet and infrared spectra of the resulting solution (after filtration from the mercuric salts) showed absorption bands characteristic of known hypobromites. After exposure of the solution to light, the infrared spectrum had undergone distinct changes to give absorption bands suggestive of the bromohydrin VII. When the hypobromite solution, prepared as above, was treated with hydrogen bromide before exposure to light, bicyclic ether formation was suppressed, only alcohol I (X = H) (and olefins) being formed on irradiation; hydrogen bromide apparently reverses hypobromite formation. Finally hypobromite I (X = Br), formed by an alternative route by the action of an aqueous solution of hypobromous acid on 1,3,3-trimethylcyclohexanol (I, X = H) (two-phase system), gave rise to the same products as those formed from the mercuric oxide-bromine reaction, albeit in different relative yields.

The intermediacy of the bromohydrin has been established by spectroscopic techniques as well as by its conversion, on treatment with silver oxide, to the bicyclic ether II. The infrared spectrum of an irradiated hypobromite solution contained bands characteristic¹⁶ of O-H and C-Br stretching frequencies at 2.9 and 14.5 μ , respectively. The structure of the bromohydrin was established conclusively, after evaporation of the pentane solvent from irradiated hypobromite, by its nuclear magnetic resonance spectrum. The spectrum was consistent (although the bromohydrin was obviously contaminated with olefins) with the assigned structure VII, and in particular had a doublet, centered at 3.7 p.p.m. (tetramethylsilane), characteristic¹⁷ of

(14) The intramolecular nature of a related process, the light-catalyzed reaction of *t*-alkyl hypochlorites to give δ -chloroalcohols, has been convincingly established: C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1597 (1963).

(15) In a recent publication indirect evidence has been provided that a bromohydrin serves as an intermediate in a similar reaction: M. Akhtar and D. H. R. Barton, *ibid.*, **86**, 1528 (1964).

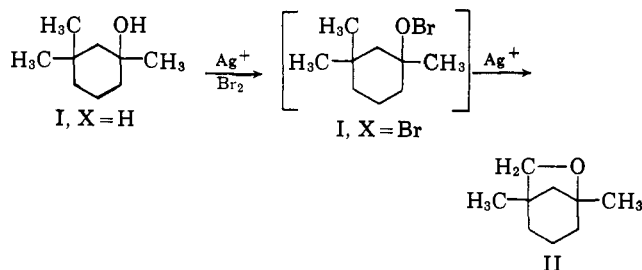
(16) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 328.

(17) L. M. Jackman, "Nuclear Magnetic Resonance Spectroscopy," The Macmillan Co., New York, N. Y., 1959, p. 53.

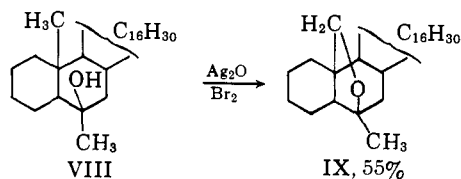
the signal of a proton on a methylene carbon to which bromine is bonded.¹⁸

The photochemical conversion of hypobromite to bromohydrin is thought to be intramolecular. That it is not an ionic intermolecular process is made probable by the observation that it is catalyzed by light of 5800 Å., corresponding to *ca.* 49 kcal./mole of energy, far less than would be expected for a process requiring free ions in pentane solution. That it is not an intermolecular free-radical process follows from our observation that it is unaffected by the addition of thiophenol, which is recovered unchanged after irradiation. Since thiophenol has been shown to be an effective trap for the 1,3,3-trimethylcyclohexoxy radical (*vide supra*), it is concluded that free radicals are not involved in the transformation.

Free Cation Decomposition of Hypobromite I (X = Br) to Bicyclic Ether II.—Silver salts catalyze the decomposition of 1,3,3-trimethylcyclohexyl hypobromite (I, X = Br)¹⁹ to bicyclic ether II, even in the absence of light. Indeed we have found that preformation of the hypobromite is not necessary since *the ether II is formed directly (75% based on recovered starting material) in the absence of light when a pentane solution of 1,3,3-trimethylcyclohexanol (I, X = H) is treated with bromine and silver oxide at room temperature for 30 min.* Presumably the hypobromite I (X = Br) serves as an intermediate in this transformation. The only other organic products observed were trace amounts of the olefins III and IV.



The reaction appears to be quite general for tertiary alcohols. Thus 6 α -methylcholestan-6 β -ol (VIII)²⁰ gives in 55% yield by the same procedure 6 α -methyl-6,19-



oxidocholestan-6-ol (IX); the acyclic alcohol 2-methylpentan-2-ol (X) furnishes 2,2-dimethyltetrahydrofuran (XI) in 50% yield.

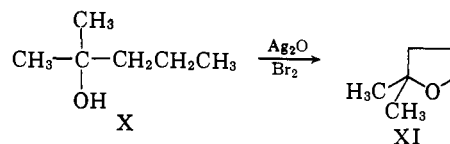
(18) The doublet is shifted from that observed in the spectrum of authentic bicyclic ether.

(19) Prepared *in situ* by the action of bromine and mercuric oxide on a pentane solution of the alcohol I (X = H).

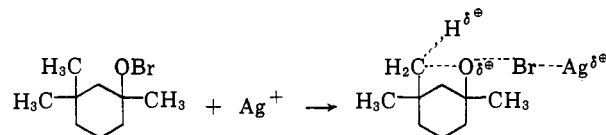
(20) Prepared by the addition of the methyl Grignard reagent to cholestan-6-one. Note that the success of the ring closure reaction confirms the 6 β -orientation assigned to the alcohol function in VIII and, by analogy, that the configurations tentatively assigned by one of us (R. A. S.) to the products of addition of various Grignard reagents to cholestan-3 β -ol-6-one acetate are incorrect.²¹ These adducts should be formulated as 6 α -R-3 β ,6 β -cholestandiols.²²

(21) R. A. Sneed, *J. Am. Chem. Soc.*, **80**, 3971, 3982 (1958).

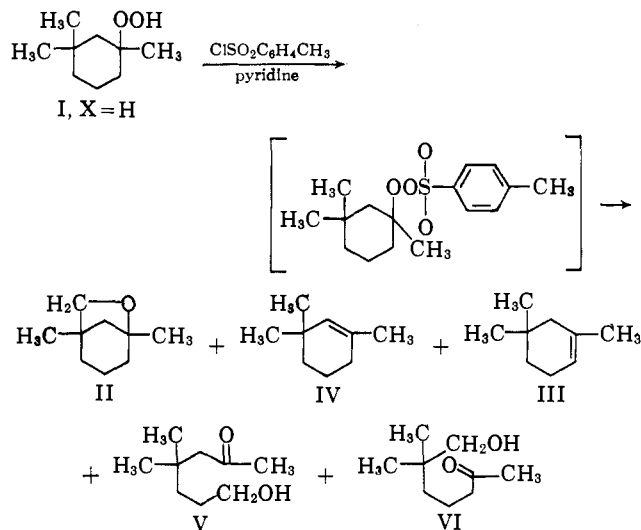
(22) This conclusion had earlier been reached by others: M. Davis and G. H. R. Summers, *J. Chem. Soc.*, 4707 (1960), and M. Shiota, *Chem. Abstr.*, **51**, 17969 (1957).



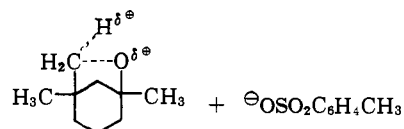
The catalytic function of silver ion is almost certainly the electrophilic removal of bromine from hypobromite to form silver bromide and a species containing some positive charge resident upon oxygen.²³ To what extent the insertion process is synchronous with the formation of silver bromide cannot as yet be answered.



Ion-Pair Decomposition of *p*-Toluenepersulfonate I (X = OSO₂C₆H₄CH₃) to Bicyclic Ether II.—The reported formation in 5–10% yield of bicyclic ether II from reaction of 1,3,3-trimethylcyclohexyl hydroperoxide (I, X = OH) with *p*-toluenesulfonyl chloride in pyridine has been confirmed.^{8,9} The reaction undoubtedly proceeds *via* the persulfonate intermediate I (X = OSO₂C₆H₄CH₃ = OTs) which we have been unable to isolate. The major products of the reaction are the keto alcohols V and VI along with lesser amounts of the olefins III and IV previously encountered as by-products of the photochemical decomposition of the hypobromite I (X = Br) (*vide supra*). As suggested by Corey and White,⁹ the reaction of the persulfonate to form bicyclic ether is almost certainly



heterolytic in character, possibly proceeding *via* an ion-paired transition state or intermediate. It will

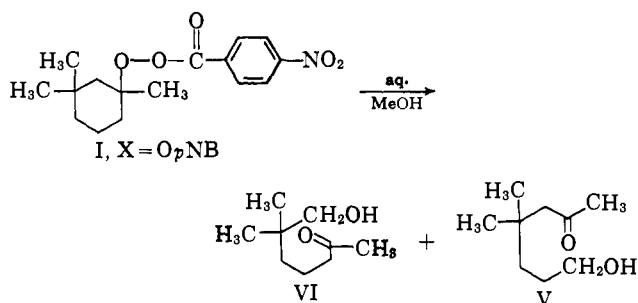


(23) Although it is conceivable that the catalytic function of silver ion is the reduction of the hypobromite to 1,3,3-trimethylcyclohexoxy radical with its concomitant oxidation to Ag⁺, analogous to the cuprous ion reduction of hydroperoxides, the extremely unfavorable electrode potential²⁴ (Ag⁺ → Ag⁰ + eE° = -1.98 v.) makes this unlikely. Furthermore, added thiophenol has no effect on the reaction, being recovered unchanged although it is known to be an effective radical scavenger (*vide supra*).

(24) T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1952, p. 284.

be noted that this species differs from that observed in the silver ion catalyzed decomposition of the hypobromite I ($X = \text{Br}$), for with the persulfonate the leaving group is a negative ion whereas with the hypobromite it is effectively neutral silver bromide. Perhaps the differing product distributions observed with these two reactions, both of which presumably involve a form of cationic oxygen, are associated with this difference. Further discussion of this point will be deferred until a later section.

Ion-Pair Decomposition of *p*-Nitroperbenzoate (I, $X = \text{O}_2\text{CC}_6\text{H}_4\text{NO}_2 = \text{O}_p\text{NB}$).—In contrast to the derivatives of 1,3,3-trimethylcyclohexanol previously discussed, all of which gave varying but isolable amounts of the bicyclic ether II on decomposition, the *p*-nitroperbenzoate ester of this system gave only the keto alcohols V and VI on decomposition in aqueous methanol.²⁵ This solvolysis reaction proved to be



quite solvent-sensitive, the steady first-order rate constant increasing by a factor of 1.49 at 51.2° on passing from 90 to 80 vol. % aqueous methanol. Kinetic data are summarized in Table I.

TABLE I
DECOMPOSITION OF 1,3,3-TRIMETHYLCYCLOHEXYL
p-NITROPERBENZOATE IN AQUEOUS METHANOL AT 51.2°

Solvent, vol. %	[Perester] × 10 ²	<i>k</i> , sec. ⁻¹ × 10 ⁴
100	7.94	1.41 ± 0.12
90	2.40	3.36 ± .18
90	3.23 ^a	3.43 ± .23
80	1.98	5.03 ± .13

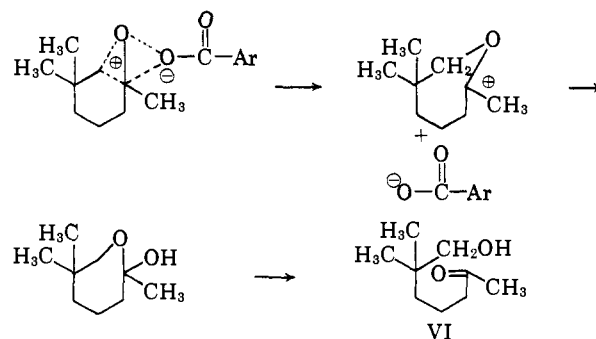
^a With 0.030 *M* perchloric acid added.

That the solvolysis is proceeding *via* an ionic transition state is certain. In view of this fact and of the similarity in kind of the products of this reaction to that of the well-studied rearrangement of the *p*-nitrobenzoate of 9-decalyl hydroperoxide (Criegee reaction),¹³ it is probable that the reactions are similar in mechanism. Application of the accepted mechanism of the Criegee rearrangement to the solvolysis of 1,3,3-trimethylcyclohexyl *p*-nitroperbenzoate (I, $X = \text{O}_p\text{NB}$) predicts the ultimate formation of the observed keto alcohols VI and V, the former *via* an ion-paired transition state in which C_2 -migration to incipient positive oxygen is synchronous with the heterolytic cleavage of the oxygen-oxygen bond. An analogous migration of C_6 would of course result in the formation of keto alcohol V.²⁶

(25) Thermal decomposition in boiling bromobenzene did furnish bicyclic ether II.

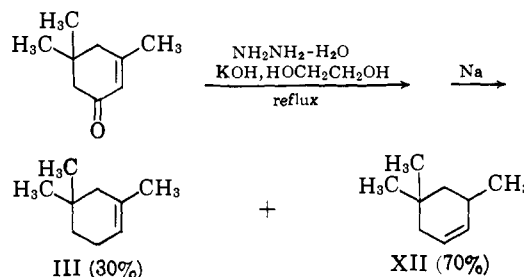
(26) Solvolysis of the *p*-nitrobenzoate of 9-decalyl hydroperoxide gave, as an isolable intermediate, the *p*-nitrobenzoate ester of the rearranged hemiacetal.²⁷ The analogous esters have not been isolated in the present work; if formed they presumably solvolyze directly to the hemiacetals.

(27) R. Criegee, *Ber.*, **77**, 722 (1944).



The clean formation of the keto alcohols, unaccompanied by bicyclic ether, from the solvolysis of the *p*-nitroperbenzoate (I, $X = \text{O}_p\text{NB}$) is to be contrasted with the lesser specificity of the *p*-toluenepersulfonate (I, $X = \text{OTs}$) decomposition where both bicyclic ether and keto alcohols, together with other products, were formed. Since both reactions are presumed to proceed by way of ion-pair transition states, the difference may lie in the considerably greater reactivity of the persulfonate, resulting in decreased selectivity. On the other hand, the third ionic process considered in this work, the silver ion catalyzed decomposition of the hypobromite I ($X = \text{Br}$), gives only the bicyclic ether II. This may be associated with the non-ion-pair character of the transition state since the leaving group in this case is effectively neutral silver bromide.

Structure Determinations.—1,5,5-Trimethylcyclohexene (III) was synthesized by the method of Alkonyi.²⁸ Microanalytical and spectrographic data confirmed the assigned structure.



The structure assigned to 4,4-dimethylheptan-6-on-1-ol (V) was confirmed by conversion of a mixture of 4,4-dimethylheptan-6-on-1-ol (V) and 2,2-dimethylheptan-6-on-1-ol (VI) to the corresponding keto esters XV and XVI, which could be separated by vapor phase chromatography. The synthetic scheme is outlined in Fig. 1. Thus a mixture of the keto alcohols V and VI, isolated by vapor phase chromatography from the solvolysis of 1,3,3-trimethylcyclohexyl *p*-nitroperbenzoate, was oxidized by Jones reagent³⁰ to the corresponding keto acids XIII and XIV which were in turn esterified by diazomethane to

(28) Alkonyi²⁹ reports only 1,5,5-trimethylcyclohexene (III) as a product of this reaction. We have found that vapor phase chromatography, using adiponitrile as a substrate, separates the product mixture at room temperature into 1,5,5-trimethylcyclohexene (III) and 3,5,5-trimethylcyclohexene (XII). The nuclear magnetic resonance spectrum of 1,5,5-trimethylcyclohexene (III) shows seven allylic protons as compared to three allylic protons in 3,5,5-trimethylcyclohexene (XII). The infrared spectrum of III has ν_{max} at 6.0 and 12.5 μ , whereas the infrared spectrum of XII has ν_{max} at 6.1 μ .

(29) I. Alkonyi, *Ber.*, **94**, 2486 (1961).

(30) A. Bowers, T. G. Halsall, E. R. H. Jones, and (in part), A. J. Lenin, *J. Chem. Soc.*, 2548 (1953).

give a mixture of the corresponding keto esters XV and XVI, separated by vapor phase chromatography. The microanalytical and spectroscopic data of the keto esters were in agreement with the structural assignment. One of these keto esters, 4,4-dimethylheptan-6-on-1-oic acid methyl ester (XV), was synthesized unambiguously for comparison by ozonolysis of 1,3,3-trimethylcyclohexene (III), obtained as described above,²⁹ to the keto acid XIII, followed by esterification (diazomethane) to the keto ester XV. The identity of the products obtained by these two sequences of reactions, one from the 1,3,3-trimethylcyclohexyl *p*-nitroperbenzoate (I, X = *Op*NB) solvolysis and the other by unambiguous synthesis, was established by identical retention times on a Carbowax column and by identical infrared spectra. Mechanistic considerations indicate that the second keto alcohol VI isolated from the perbenzoate reaction would lead on oxidation and esterification to the isomeric 2,2-dimethylheptan-6-on-1-oic acid methyl ester (XVI). The microanalytical data and nuclear magnetic resonance spectra of the two keto esters were found to be essentially identical; they do, however, differ in the fingerprint region of the infrared spectra and in their vapor phase chromatographic behavior.

Experimental³¹

1,3,3-Trimethylcyclohexyl Hydroperoxide.—To a solution containing 0.5 ml. of water, 4.5 ml. of 98% hydrogen peroxide, and 0.1 ml. of concentrated sulfuric acid³² in a 100-ml. three-necked flask, cooled in ice and stirred with a magnetic stirrer, was added slowly 2.2 g. of finely pulverized 1,3,3-trimethylcyclohexanol.^{33,34} The heterogeneous mixture was allowed to stir at ice temperatures for 9 hr. After this time 30 ml. of water was added and the resulting solution was extracted immediately with 35–37° petroleum ether. The petroleum ether layer was dried over anhydrous sodium carbonate and was then allowed to evaporate, yielding a clear viscous liquid.

An H^1 n.m.r. spectrum (deuteriochloroform) of the material showed CH_3 peaks at 0.90, 1.10, and 1.20, $-CH_2-$ signals from 1.20 to 1.90, and a quartet centered at 3.5 p.p.m. The 1,3,3-trimethylcyclohexyl hydroperoxide was not further characterized.

The experimental hazards involved with the use of 98% hydrogen peroxide were found to be minimized by the addition of concentrated sulfuric acid, before the addition of any organic materials, and by the use of carefully purified alcohol.

1,3,3-Trimethylcyclohexyl Hydroperoxide in Refluxing Cyclohexane with Cuprous Chloride.³⁵—To a solution containing 25 ml. of cyclohexane and 540 mg. of 1,3,3-trimethylcyclohexyl hydroperoxide was added 1.042 g. of cuprous chloride. The suspension, while being stirred magnetically, was allowed to reflux for 24 hr. After this time it was cooled to room temperature and filtered to remove the inorganic salts. The cyclohexane was removed under vacuum and the products were analyzed by vapor phase chromatography. Vapor phase chromatographic analysis indicated as products 6-oxa-1,5-dimethyl[3.2.1]bicyclooctane (II) and 1,3,3-trimethylcyclohexanol (I, X = H). In a control experiment the 1,3,3-trimethylcyclohexyl hydroperoxide was shown to be stable under the reaction conditions in the absence of cuprous chloride.

(31) Boiling points and melting points are uncorrected. Infrared spectra were obtained with a Perkin-Elmer Model 137B Infracord spectrophotometer with sodium chloride optics. Nuclear magnetic resonance spectra were determined on a Varian Model A-60 (60 Mc.) spectrometer using tetramethylsilane as the internal reference.

(32) W. A. Milas and L. H. Perry, *J. Am. Chem. Soc.*, **68**, 1938 (1946).

(33) G. B. Payne, *J. Org. Chem.*, **24**, 719 (1959).

(34) P. S. Wharton and D. H. Bohlen, *ibid.*, **26**, 3615 (1961).

(35) In this and a few other early experiments dealing with the hydroperoxide, small quantities of cyclohexene were added to the reaction mixture. Since it has been shown that the experimental conclusions of interest for the present study are the same both in the presence and absence of cyclohexene, it has been deleted from a few of the following descriptions of experiments.

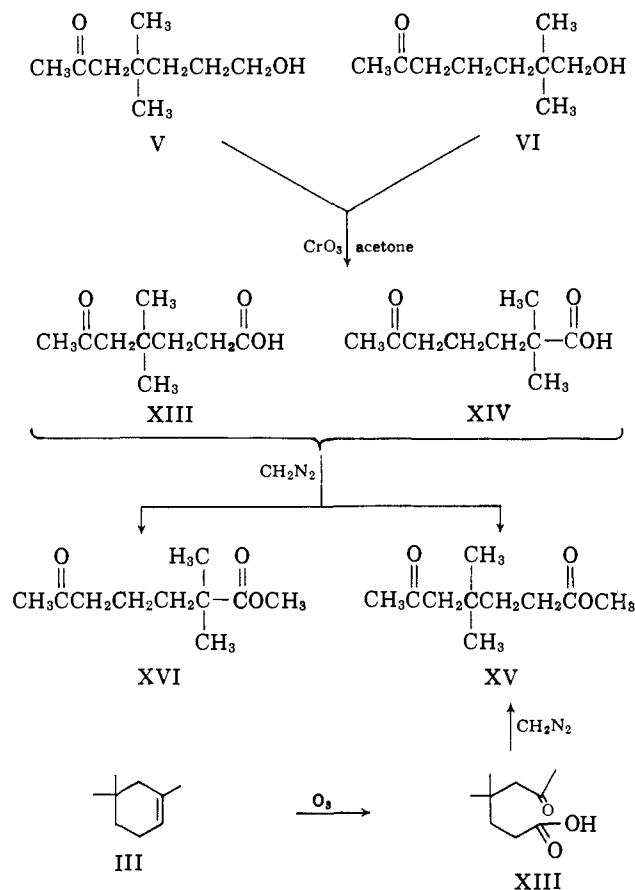


Figure 1.

1,3,3-Trimethylcyclohexyl Hydroperoxide in Refluxing Cyclohexane with Cuprous Chloride and Thiophenol (0.0066 Mole).—To a solution containing 25 ml. of cyclohexane and 530 mg. (0.0033 mole) of 1,3,3-trimethylcyclohexyl hydroperoxide was added 1.907 g. of cuprous chloride and 0.5 ml. (0.0066 mole) of thiophenol. The solution was heated to reflux temperature and was allowed to reflux, with magnetic stirring, for 24 hr. After this time it was allowed to cool and was then filtered to remove the copper salts. The filtrate was analyzed by infrared spectroscopy and vapor phase chromatography. Infrared spectroscopy indicated the presence of diphenyl disulfide and the absence of thiophenol. Vapor phase chromatography indicated the presence of 6-oxa-1,5-dimethyl[3.2.1]bicyclooctane and 1,3,3-trimethylcyclohexanol. In a separate experiment it was shown that cuprous chloride does not react with thiophenol in the absence of hydroperoxide.

1,3,3-Trimethylcyclohexyl Hydroperoxide in Refluxing Cyclohexane with Cuprous Chloride and Thiophenol (0.014 Mole).—To a solution containing 520 mg. (0.0033 mole) of 1,3,3-trimethylcyclohexyl hydroperoxide and 25 ml. of cyclohexane was added 662 mg. of cuprous chloride and 1 ml. (0.014 mole) of thiophenol. The solution was heated to reflux, while being stirred magnetically, and was allowed to reflux for 24 hr. The resulting deep blue reaction mixture was allowed to cool and was filtered to remove the inorganic salts. The solution was analyzed by vapor phase chromatography both before and after filtration, giving no evidence for the formation of the bicyclic ether II. Other than solvent, 1,3,3-trimethylcyclohexanol was the only product indicated on vapor phase chromatography. Analysis of the filtrate by infrared spectroscopy indicated diphenyl disulfide and no thiophenol.

Reaction of 6-Oxa-1,5-dimethyl[3.2.1]bicyclooctane with Hydrobromic Acid.—To a solution containing 1 ml. of 6-oxa-1,5-dimethyl [3.2.1]bicyclooctane (II) (v.p.c. pure) and 5 ml. of pentane was added 2 ml. of hydrobromic acid. The solution was stirred for 12 hr. at room temperature. Analysis of the solution at the beginning and at the end of this time by vapor phase chromatography showed no change; *i.e.*, the amount of bicyclic ether II did not decrease, nor were there any other products apparently formed.

Light-Catalyzed Decomposition of 1,3,3-Trimethylcyclohexyl Hypobromite.—To a solution containing 567 mg. of 1,3,3-trimethylcyclohexanol and 30 ml. of pentane was added 2.635 g. of mercuric oxide and 0.5 ml. of bromine. The reaction was allowed to proceed with stirring for 2 hr. The mixture was filtered to remove the mercuric salts and the pentane was allowed to evaporate partially. The preceding operations were all carried out in the dark. The reaction mixture was then transferred to a lighted room and aliquots were withdrawn periodically and analyzed by vapor phase chromatography to determine the ratio of products present. There was no apparent change in the product ratio with time. Vapor phase chromatography showed that 6-oxa-1,5-dimethyl[3.2.1]bicyclooctane (II) was present in *ca.* 60% yield, the olefins 1,5,5-trimethylcyclohexene (III) and 1,3,3-trimethylcyclohexene (IV) were present in *ca.* 30% yield, and 4,4-dimethylheptan-6-on-1-ol (V) was present in *ca.* 10% yield.

Decomposition of 1,3,3-Trimethylcyclohexyl Hypobromite at Varying Wave Lengths of Light.—To a solution containing 444 mg. of 1,3,3-trimethylcyclohexanol and 15 ml. of pentane was added with stirring 3.5 g. of mercuric oxide and 0.2 ml. of bromine. After 10 min. of further stirring the solution was filtered to remove the mercuric salts. The solution was then transferred to a 2-dm. jacketed polarimeter tube. All of the preceding operations were carried out in the dark. After irradiation for 1.5 hr. in a Rudolph polarimeter at 2810 Å. the solution was removed from the tube in the dark and the product mixture was analyzed by infrared spectroscopy. The infrared spectrum indicated the presence of 1,3-dimethyl-3-bromomethylenecyclohexan-1-ol (VII), with absorption bands of 1,3,3-trimethylcyclohexyl hypobromite virtually absent. Two similar experiments, differing only in that irradiation of wave lengths 3660 and 5790 Å. was used, gave similar results.

1,3,3-Trimethylcyclohexyl Hypobromite. Infrared Analysis.—To a stirred solution, in a dark room, containing 859 mg. of 1,3,3-trimethylcyclohexanol and 30 ml. of pentane, was added 5.327 g. of mercuric oxide. To this mixture was then added 0.5 ml. of bromine and the mixture was allowed to stir briefly. The reaction mixture was filtered to remove the mercuric salts and the filtrate was used to determine an infrared spectrum. All reactions were carried out in a dark room illuminated by a 25-watt bulb, protected by a Kodak Safelight Filter-Wratten-Series OA. Solutions for infrared spectroscopic analysis were prepared in the dark and were protected as much as possible from light by wrapping them in aluminum foil. After determination of the spectrum, the reaction mixture was transferred to a lighted room for a 30-min. period after which a spectrum was again obtained. A change in relative peak intensities was apparent, particularly an increase in the intensity at 9.8 μ , indicating that light had caused decomposition of the hypobromite to occur.

1,3,3-Trimethylcyclohexyl Hypobromite. Ultraviolet Analysis.—To a solution, in a dark room, containing 1.035 g. of 1,3,3-trimethylcyclohexanol and 25 ml. of carbon tetrachloride (Baker Spectrophotometric Grade) was added 5.39 g. of mercuric oxide and, with stirring, 0.5 ml. of bromine. The solution was filtered to remove the mercuric salts, and the ultraviolet spectrum of the filtrate was obtained. All of the preceding operations were carried out in the dark. It was necessary to dilute the solution to determine its ultraviolet maxima; therefore, the extinction coefficient was not obtained as the concentration of the solution was uncertain. The 1,3,3-trimethylcyclohexyl hypobromite had an ultraviolet maximum at 2800 Å. with a weak shoulder at 3400 Å.³⁶

Reaction of 1,3,3-Trimethylcyclohexyl Hypobromite with Hydrobromic Acid.—To a solution containing 2.26 g. of 1,3,3-trimethylcyclohexanol and 50 ml. of pentane was added with stirring 3.6 g. of mercuric oxide and 0.6 ml. of bromine, the addition being carried out in a dark room. The reaction was allowed to proceed for 3 hr. at room temperature and was then filtered twice to remove the mercuric salts. To a portion of this solution was added 1 ml. of hydrobromic acid. All operations to this point were carried out in the dark. After 3 hr., vapor phase chromatographic analysis of the reaction mixture indicated the absence of the bicyclic ether; only the olefinic peaks were apparent. After 24 hr. other peaks not previously obtained were apparent on vapor phase chromatographic analysis.

Decomposition of 1,3,3-Trimethylcyclohexyl Hypobromite with Added Thiophenol.—To a solution containing 915 mg. of 1,3,3-trimethylcyclohexanol and 30 ml. of pentane was added with

stirring 4.34 g. of mercuric oxide and 0.5 ml. of bromine. After the mixture had been stirred for 15 min. it was filtered to remove the mercuric salts and was then analyzed by vapor phase chromatography. Thiophenol (1.0 ml.) was then added and the solution was again analyzed by vapor phase chromatography. All of the preceding operations were carried out in the dark. The reaction mixture was then taken into the light and aliquots were withdrawn periodically and analyzed by vapor phase chromatography. There was no change in product composition with time. After evaporation of the solvent, an infrared spectrum of the product mixture was obtained. The spectrum showed no evidence of diphenyl disulfide; only bands characteristic of thiophenol and of the products of the 1,3,3-trimethylcyclohexyl hypobromite decomposition were apparent.

1,3,3-Trimethylcyclohexyl Hypobromite from Hypobromous Acid.³⁷—To a solution containing 0.04 mole of bromine in *ca.* 200 ml. of distilled water was added concentrated silver nitrate solution, in a dark room, until the formation of silver bromide had apparently ceased. The solution was filtered to remove the silver bromide which had formed and was used directly in the following operation. To the solution prepared above containing hypobromous acid was added a solution of 2.0 g. of 1,3,3-trimethylcyclohexanol dissolved in 50 ml. of pentane. Reaction was allowed to proceed for 30 minutes in the dark. After this time the layers were separated and the organic layer was dried over anhydrous sodium carbonate. The solution was transferred to the light and, after *ca.* 1 hr., the pentane was allowed to evaporate partially. The resulting product mixture was analyzed by vapor phase chromatography. Product analysis indicated the presence of the olefins 1,5,5-trimethylcyclohexene and 1,3,3-trimethylcyclohexene, of 4,4-dimethylheptan-6-on-1-ol, and of 6-oxa-1,5-dimethyl[3.2.1]bicyclooctane, as well as an unstable bromine-containing product, sometimes observed when mercuric oxide was used as a catalyst. The product mixture had more olefin present than is usually observed when mercuric oxide is used to generate the intermediate hypobromite.

1,3-Dimethyl-3-Bromomethylenecyclohexan-1-ol. N.m.r. Analysis.—To a solution containing 400 mg. of 1,3,3-trimethylcyclohexanol and 20 ml. of pentane was added 2.5 g. of mercuric oxide. The solution was stirred magnetically in a darkened room and to it was added 0.2 ml. of bromine. The solution was then filtered to remove the mercuric salts, and the solution was then brought into a lighted room and allowed to stand for 2 hr. The pentane was evaporated and the solution was analyzed immediately by nuclear magnetic resonance spectroscopy. Nuclear magnetic resonance indicated a doublet at 3.7 p.p.m. which differs from the quartet centered at 3.5 p.p.m. characteristic of the bicyclic ether II. The spectrum indicated the presence of olefins as contaminants.

1,3-Dimethyl-3-Bromomethylenecyclohexan-1-ol. Infrared Analysis.—To a solution containing 427 mg. of 1,3,3-trimethylcyclohexanol and 30 ml. of pentane was added 5.79 g. of mercuric oxide in a dark room. To this mixture was then added 0.2 ml. of bromine and reaction was allowed to proceed for 30 min. The solution was filtered to remove the mercuric salts and the filtrate was analyzed by infrared spectroscopy. The infrared spectrum showed no bands in the 3.0- and 14.5- μ region, but showed a strong peak at 8.5 μ (hypobromite). The 1,3,3-trimethylcyclohexyl hypobromite solution was then cooled to Dry Ice temperatures and at this point was brought into a lighted room and, in addition, irradiated with an ultraviolet Blaklight for 2 hr. The solution was then returned to the dark room and an infrared analysis again made of the solution. Strong bands were present at 2.9, 8.4, 10.4, 11.0, and 14.5 μ , and the strong band indicative of the 1,3,3-trimethylcyclohexyl hypobromite at 8.5 μ had disappeared. The bands at 2.9 and 14.5 μ were attributed to O-H and C-Br stretching bands, respectively.¹⁶ The solution was then allowed to warm to room temperature and was again irradiated with light at room temperature for 6 hr. There was no further change in the spectrum. To a portion of the solution was then added silver oxide, the solution was filtered to remove the silver salts, and the filtrate was analyzed by infrared spectroscopy. The spectrum now indicated the presence of the bicyclic ether II with particularly strong absorption at 9.8 μ , the bands at 2.9 and 14.5 μ having essentially disappeared.

Reaction of 1,3,3-Trimethylcyclohexanol with Silver Oxide and Bromine.—To a solution, in a dark room, containing 2.75 g. of 1,3,3-trimethylcyclohexanol and 100 ml. of pentane was added

(36) M. Anbar and I. Dostrovsky, *J. Chem. Soc.*, 1105 (1954).(37) C. Walling and A. Padwa, *J. Org. Chem.*, **27**, 2976 (1962).

with stirring 8.0 g. of silver oxide. The mixture was allowed to stir briefly before 1.0 ml. of bromine was added. After the reaction had proceeded for 30 min. the solution was filtered to remove the silver salts. The solids were washed with pentane, which was then added to the filtrate. Evaporation of solvent furnished an oil which was purified by chromatography on alumina. Chromatography yielded traces of olefins (pentane), followed by 1.5 g. of bicyclic ether II (pentane). The final fractions contained 0.76 g. of 1,3,3-trimethylcyclohexanol (ether). The total yield of II is thus 75%, based on recovered starting material.

Other experiments provided evidence that the bicyclic ether had formed in the dark.

Analogous experiments have indicated that the reaction proceeds with silver nitrate and silver acetate as well as silver oxide.

Reaction of 1,3,3-Trimethylcyclohexyl Hypobromite with Silver Oxide and Thiophenol.—To a stirred solution, in a dark room, containing 502 mg. of 1,3,3-trimethylcyclohexanol and 30 ml. of pentane, was added 3.65 g. of mercuric oxide, followed by 0.3 ml. of bromine. The reaction proceeded for 30 min. at room temperature and the reaction mixture was then filtered to remove the mercuric salts. To the stirred filtrate was then added 1 ml. of thiophenol, followed by 3.98 g. of silver oxide. After stirring magnetically for 30 min., the reaction mixture was filtered to remove the silver oxide and silver bromide which had formed. The experiment to this point was carried out in the dark room under conditions previously described. Analysis of the product mixture by vapor phase chromatography indicated the presence of the products generally observed; *i.e.*, olefin III, bicyclic ether II, and some recovered starting material (I, X = H) were present. Analysis of the product mixture by infrared spectroscopy indicated the presence of thiophenol and the apparent absence of diphenyl disulfide.

Reaction of 2-Methylpentan-2-ol with Silver Oxide and Bromine.—To a solution in a dark room containing 1.6 g. of 2-methylpentan-2-ol (X) (Eastman) and 30 ml. of pentane was added with stirring 5.10 g. of mercuric oxide, 2.37 g. of silver oxide, and 1.0 ml. of bromine. The solution was allowed to stir for 10 min. and was then filtered to remove the mercuric and silver salts. After the pentane had evaporated, the product mixture was analyzed by vapor phase chromatography and infrared spectroscopy. In addition to solvent and recovered starting material, vapor phase chromatography indicated three products in the relative percentages of 15:50:35.

The first component, present in *ca.* 15% yield, was identified as *n*-propyl bromide by comparison of its nuclear magnetic resonance and infrared spectra with those of an authentic sample.

An H^1 n.m.r. spectrum (carbon tetrachloride) of propyl bromide showed signals at 1.0 (triplet), 1.85 (sextet), and 3.35 p.p.m. (triplet).

The second component, present in *ca.* 50% yield, was identified as 2,2-dimethyltetrahydrofuran (XI) from its microanalytical data and its infrared and nuclear magnetic resonance spectra. An H^1 n.m.r. spectrum (carbon tetrachloride) of 2,2-dimethyltetrahydrofuran showed signals at 1.25 (singlet), 1.5 to 2.1 (multiplet), and 3.8 p.p.m. (triplet).

Anal. Calcd. for $C_6H_{12}O$: C, 71.94; H, 12.07. Found: C, 71.24; H, 12.23.

The third component, present in *ca.* 35% yield, was found to be a mixture of two compounds which could not be separated. A Beilstein test indicated that at least one contained bromine. A comparison of the nuclear magnetic resonance spectrum of the mixture with that of an authentic sample of isopropyl bromide would suggest that it is one of the components.

An H^1 n.m.r. spectrum (carbon tetrachloride) of the mixture showed signals at 1.0 (triplet), 1.3 to 2.3 (multiplet), 1.70 (doublet), and 4.1 (octet). An H^1 n.m.r. spectrum of authentic isopropyl bromide showed signals at 1.70 (doublet), 1.3 to 2.3 (multiplet), and 4.1 (octet).

6 α -Methylcholestan-6 β -ol (VIII).—6 α -Methylcholestan-6 β -ol (VIII) was prepared by the addition of methylmagnesium iodide to cholestan-6-one.³⁸ To a previously prepared solution of the Grignard reagent (prepared by the dropwise addition of a solution of 4.0 ml. of methyl iodide in 50 ml. of anhydrous ether to a stirred suspension of 0.35 g. of magnesium turnings in 20 ml. of ether) was added a solution containing 1.5 g. of cholestan-6-one³⁸ dissolved in 50 ml. of ether. The addition was at a rate sufficient to maintain gentle reflux. The stirring was continued for *ca.* 2.5 hr.

after the addition had been completed and the excess Grignard reagent was then decomposed by the dropwise addition of methanol. The precipitated salts were dissolved by the addition of saturated ammonium chloride solution. The ethereal layer was isolated, washed with water, and the ether was evaporated. Crystallization was effected from ethanol, furnishing 6 α -methylcholestan-6 β -ol (VIII), m.p. 99.5–101°, $[\alpha]^{27.5}_D +22.3^\circ$ (ethanol) $[\alpha]^{25}_D +25.1^\circ$ (chloroform). An H^1 n.m.r. spectrum (carbon tetrachloride) showed principal peaks (CH_3) at 0.7, 0.8, 0.92, 0.97, 1.05, with $-CH_2-$ signals from 0.7 to 2.1 p.p.m.

Anal. Calcd. for $C_{28}H_{50}O$: C, 83.51; H, 12.52. Found: C, 83.38; H, 12.68.

6 α -Methylcholestan-6,19-Oxide (IX).—To a solution containing 445 mg. of 6 α -methylcholestan-6 β -ol in 30 ml. of pentane was added 2.069 g. of silver oxide and 8.495 g. of mercuric oxide. After the solution had stirred briefly, 100 μ l. of bromine was added and the mixture was stirred in the dark for 0.5 hr. The mixture was filtered to remove the solid salts and the pentane was allowed to evaporate, yielding a yellow oil. Dilution with acetone furnished 243 mg. (55%) of 6 α -methylcholestan-6,19-oxide. Recrystallization from ether-methanol gave 6 α -methylcholestan-6,19-oxide, m.p. 83–84°, $[\alpha]^{26.5}_D +14.7^\circ$ (chloroform); infrared: ν_{max} 9.8 μ . An H^1 n.m.r. spectrum (carbon tetrachloride) of the oxide showed principal peaks (CH_3) at 0.7, 0.8, 0.9, 1.05, with $-CH_2-$ signals from 0.70 to 1.80 with a doublet at 3.5 p.p.m.

Anal. Calcd. for $C_{28}H_{48}O$: C, 83.93; H, 12.01. Found: C, 83.84; H, 12.16.

Reaction of 1,3,3-Trimethylcyclohexyl Hydroperoxide with *p*-Toluenesulfonyl Chloride.—To a solution containing 15 ml. of ether and 10 ml. of butyllithium (1.5 *M* in hexane) at Dry Ice temperatures was added 1.5 g. of 1,3,3-trimethylcyclohexyl hydroperoxide in 10 ml. of ether. After a short time 1.9 g. of *p*-toluenesulfonyl chloride, dissolved in 10 ml. of ether, was added dropwise and reaction was allowed to proceed for 3 hr. at Dry Ice temperatures.

After this time the solution was filtered to remove the solid material which had formed, the filtrate being collected at Dry Ice temperatures. The filtrate was kept at 0° overnight, during which time additional precipitate formed. Upon isolation, the precipitate proved to be *p*-toluenesulfonyl chloride, by comparison of its infrared spectrum with that of an authentic sample. Additional solid was isolated at Dry Ice temperatures, which upon isolation proved to be a mixture of 2,2-dimethylheptan-6-on-1-ol and 4,4-dimethylheptan-6-on-1-ol. The keto alcohols V and VI were identified by comparison of vapor phase chromatography retention times and by comparison of the infrared spectrum of a mixture of authentic samples. The solvent was allowed to evaporate and the product mixture was analyzed by vapor phase chromatography, indicating, in addition to the keto alcohols, 1,5,5-trimethylcyclohexene, 1,3,3-trimethylcyclohexene, and 6-oxa-1,5-dimethyl[3.2.1]bicyclooctane. Two additional products were indicated, but were in insufficient amount for identification.

1,3,3-Trimethylcyclohexyl *p*-Nitroperbenzoate.—To 15 ml. of anhydrous ether was added with a syringe 10 ml. of butyllithium in hexane (1.5 *M*). To this solution maintained at ice temperatures was added 1,3,3-trimethylcyclohexyl hydroperoxide, followed after a short time by a solution of 2.1 g. of *p*-nitrobenzoyl chloride dissolved in 15 ml. of ether. A precipitate formed immediately; however, the reaction was allowed to continue for 1.5 hr. After this time the reaction mixture was filtered to remove the solid material and the filtrate was allowed to evaporate, yielding a precipitate and an oil. An infrared spectrum of the product mixture indicated the presence of unreacted 1,3,3-trimethylcyclohexyl hydroperoxide and 1,3,3-trimethylcyclohexyl *p*-nitroperbenzoate. The product mixture was washed with hexane, furnishing 1,3,3-trimethylcyclohexyl *p*-nitroperbenzoate, with the washings containing unreacted 1,3,3-trimethylcyclohexyl hydroperoxide. The product was recrystallized from ether-ethanol, furnishing 1,3,3-trimethylcyclohexyl *p*-nitroperbenzoate, m.p. 111–112.5° dec. [lit.⁹ m.p. 113.5–114° dec.], ν_{max} 5.7 μ . An H^1 n.m.r. spectrum of the material showed CH_3 peaks at 0.95, 1.10, and 1.40; $-CH_2-$ signals from 1.2 to 2.2; and aromatic H quartet centered at 8.25 p.p.m.

Solvolysis of 1,3,3-Trimethylcyclohexyl *p*-Nitroperbenzoate in Methanol.—A solution containing 2.0 g. of 1,3,3-trimethylcyclohexyl *p*-nitroperbenzoate in 125 ml. of methanol was heated under reflux for 12 hr. After this time the solution was cooled and poured into 200 ml. of water. Crystals (0.9 g.) formed in the aqueous solution and were removed by filtration. The solid material formed was found, by comparison with an authentic

(38) N. P. Matheny, Ph. D. Thesis, Purdue University, 1964.

sample of its infrared spectrum and melting point, to be *p*-nitrobenzoic acid. The filtrate obtained above was extracted repeatedly with ether and the ether extracts were combined and were dried with anhydrous sodium carbonate. The ether was allowed to evaporate and the resulting oil was chromatographed on silica gel using hexane and ether as eluents. Initial fractions (50% hexane-50% ether) contained traces of methyl *p*-nitrobenzoate, identical by comparison of its infrared spectrum with the literature spectrum of an authentic sample.⁸⁹ Later fractions (ether) contained a material which was analyzed by standard analytical methods. Infrared and nuclear magnetic resonance spectroscopy indicated the product to be a keto alcohol. Vapor phase chromatography indicated the possibility of two compounds, and this was, in later work, shown to be the case. The compounds were identified as the isomeric 2,2-dimethylheptan-6-on-1-ol (VI) and 4,4-dimethylheptan-6-on-1-ol (V). An H¹ n.m.r. spectrum (carbon tetrachloride) of the mixture showed principal peaks at 0.90 (6), multiplet from 1.0 to 1.7 (4), singlet 2.1 (3), multiplet from 2.2 to 2.6 (3), singlet 3.3 p.p.m. (2).

Decomposition of 1,3,3-Trimethylcyclohexyl *p*-Nitroperbenzoate in Bromobenzene.—A solution containing 144 mg. of 1,3,3-trimethylcyclohexyl *p*-nitroperbenzoate and 7 ml. of bromobenzene was heated to its reflux temperature within 5 min., during which time the solution developed a yellow color. After refluxing for 3 hr., the solution was allowed to cool with the subsequent development of a precipitate. The solution was then filtered, furnishing >53 mg. of *p*-nitrobenzoic acid, which was identified by comparison of its melting point and infrared spectrum with those of an authentic sample. The remaining solution was then analyzed by vapor phase chromatography, which indicated the presence of the bicyclic ether II. There was no evidence of keto alcohols V and VI in the chromatogram.

Kinetics of Solvolysis of 1,3,3-Trimethylcyclohexyl *p*-Nitroperbenzoate in Methanol Solutions.—The rates of solvolysis of 1,3,3-trimethylcyclohexyl *p*-nitroperbenzoate in methanol and aqueous methanol solutions were determined. A weighed sample (by difference) of ester was placed in a 100-ml. volumetric flask, and sufficient solvent was added to give a volume of 100 ml. Aliquots (5 ml.) were pipetted out at intervals, quenched in a mixture of 5 ml. of carbon tetrachloride and 10 ml. of distilled water, and the resulting two-phase system was titrated to the phenolphthalein end point with *ca.* 0.02 *M* sodium hydroxide while the system was stirred magnetically. A typical run is given as Table II.

TABLE II
SOLVOLYSIS OF 7.94×10^{-3} *M* 1,3,3-TRIMETHYLCYCLOHEXYL
p-NITROPERBENZOATE IN ABSOLUTE METHANOL AT 51.2°^a

Time, sec.	Base, ml.	<i>k</i> , sec. ⁻¹ × 10 ⁴
...	0.225	...
1200	.505	1.38
2400	.750	1.46
3600	.960	1.49
4800	1.145	1.53
6300	1.285	1.45
7200	1.360	1.42
9000	1.485	1.38
12600	1.645	1.29
16200	1.775	1.29
21600	1.905	1.38
97900	1.995	
∞	1.995	

$$\text{Av.} = 1.41 \pm 0.12$$

^a[NaOH] = 2.14×10^{-2} *M*; blank = 0.120 ml.; theoretical infinity titer = $1.854 + 0.120 = 1.974$ ml.; % of theory = $[(1.995 - 0.120)/1.854] \times 100 = 101.1\%$.

1,5,5-Trimethylcyclohexene (III).²²—A solution containing 50 g. (0.36 mole) of isophorone, 50 ml. of 96% hydrazine hydrate, and 30 g. of potassium hydroxide in 150 ml. of ethylene glycol was heated under reflux for 2.5 hr. and was then distilled (b.p. *ca.* 115°) affording two layers. The organic layer was removed and to it was added elemental sodium. The solution was then heated to reflux temperature. After a short time the solution was distilled at 134–135°, yielding a colorless liquid. The infrared spectrum had two olefinic peaks at 6.0 and 6.1 μ . Gas

chromatography on an adiponitrile column at room temperature separated the product mixture into two fractions which were collected.

From the nuclear magnetic resonance and infrared analyses the first olefin is assigned the structure of 3,5,5-trimethylcyclohexene (XII) and the second, 1,5,5-trimethylcyclohexene (III).

An H¹ n.m.r. spectrum of 3,5,5-trimethylcyclohexene showed CH₃– peaks at 0.90, 0.95, and 1.05 (9); –CH₂– multiplet at 1.4 (2); allylic H at 1.8 (3); and vinyl H at 5.6 p.p.m. (2). The H¹ n.m.r. spectrum of 1,5,5-trimethylcyclohexene showed a CH₃– peak at 0.95 (6); –CH₂– triplet at 1.3 (2); allylic H at 1.7 (7); and vinyl H at 5.5 p.p.m. (1).

Ozonolysis of a Mixture of 1,5,5-Trimethylcyclohexene and 3,5,5-Trimethylcyclohexene.—1,5,5-Trimethylcyclohexene (III) and 3,5,5-trimethylcyclohexene (XII) have only been separated by vapor phase chromatography. Accordingly, the product mixture obtained on Wolff–Kishner reduction of isophorone was ozonized directly. To 15 g. of a mixture of 1,5,5-trimethylcyclohexene and 3,5,5-trimethylcyclohexene (obtained as outlined above) was added 20 ml. of methylene chloride. The solution was cooled to Dry Ice temperature and ozonized for 8 hr., during which time it became thick and sirupy. Additional methylene chloride (10 ml.) was added and ozonolysis continued for 1 hr., during which time a distinct blue color developed.

The methylene chloride solution was then added to a solution containing 10 ml. of 30% hydrogen peroxide and 100 ml. of water. After being stirred for 36 hr. the solution was repeatedly extracted with ether. The ethereal extracts were combined and were washed repeatedly with sodium carbonate solution. The sodium carbonate solution was acidified with dilute hydrochloric acid and was extracted repeatedly with ether. The ethereal extracts were combined and dried with anhydrous sodium carbonate. After the ether had evaporated the solution was analyzed by infrared spectroscopy. The infrared spectrum indicated the presence of two carbonyl bands at 5.85 and 5.90 μ . The crude oil was used directly in the preparation of the methyl esters of the keto acid and diacid which were formed by ozonolysis.

Esterification of a Mixture of 4,4-Dimethylheptan-6-on-1-oic Acid and 2,4,4-Trimethylheptane-1,7-dioic Acid.—To the product mixture obtained from ozonolysis of 1,5,5-trimethylcyclohexene and 3,5,5-trimethylcyclohexene (described above) dissolved in 50 ml. of ether was added diazomethane⁴⁰ in ether until the yellow color of diazomethane persisted. The solution was allowed to stand first at ice temperature and then at room temperature until the ether had evaporated. Infrared spectroscopic analysis of the resulting product mixture indicated the presence of two carbonyl peaks and the disappearance of the broad band from 3.0 to 4.0 μ generally attributed to acids.⁴¹ The resulting product mixture was analyzed by vapor phase chromatography and was found to contain two principal peaks. The first was identified as the dimethyl ester of 2,4,4-trimethylheptane-1,7-dioic acid, arising from 3,5,5-trimethylcyclohexene. The second was identified as 4,4-dimethylheptan-6-on-1-oic acid methyl ester, arising from the 1,5,5-trimethylcyclohexene.

An H¹ n.m.r. spectrum (carbon tetrachloride) of the dimethyl ester of 2,4,4-trimethylheptane-1,7-dioic acid showed principal peaks at 0.95 (singlet), 1.1 to 2.1 (multiplet), 2.15 (singlet), and 3.6 p.p.m. (singlet).

Anal. Calcd. for C₁₁H₂₀O₄: C, 61.09; H, 9.32. Found: C, 61.32; H, 9.63.

An H¹ n.m.r. spectrum (carbon tetrachloride) of the methyl ester of 4,4-dimethylheptan-6-on-1-oic acid showed principal peaks at 1.0 (singlet), 1.1 to 1.8 (multiplet), 2.05 (singlet), 2.1 to 2.3 (multiplet), and 3.6 p.p.m. (singlet).

Anal. Calcd. for C₁₀H₁₈O₃: C, 64.49; H, 9.74. Found: C, 62.77; H, 9.39.

2,2-Dimethylheptan-6-on-1-oic Acid and 4,4-Dimethylheptan-6-on-1-oic Acid.—About 4 g. of 1,3,3-trimethylcyclohexyl *p*-nitroperbenzoate and 200 ml. of methanol were allowed to reflux for 12 hr. After this time the methanol solution was poured into water with the resultant formation of a precipitate. The precipitate was removed by filtration and the resulting methanol solution was allowed to evaporate. To the oil which was obtained on evaporation of the methanol was added *ca.* 150 ml. of acetone and then Jones⁴⁰ reagent was added until the latter was in excess (indicated by the maintenance of the orange color). The solution

(40) F. Arndt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., p. 165.

(41) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 179.

(39) "Sadler Standard Spectra," Sadler Research Laboratories, Philadelphia, Pa., 1956, No. 4899.

was allowed to stir for *ca.* 15 hr. and was then filtered to remove the chromium salts. The resulting filtrate was evaporated under vacuum, furnishing a green-white oil. The oil was dissolved in ether; the ethereal solution was washed with water, and was then dried with magnesium sulfate. Infrared spectroscopic analysis indicated a material comparable with that obtained on ozonolysis of 1,5,5-trimethylcyclohexene. The oil was used directly in the preparation of the methyl esters XV and XVI.

2,2-Dimethylheptan-6-on-1-oic Acid Methyl Ester and 4,4-Dimethylheptan-6-on-1-oic Acid Methyl Ester.—To the crude 2,2-dimethylheptan-6-on-1-oic acid and 4,4-dimethylheptan-6-on-1-oic acid obtained above was added an ethereal solution of diazomethane (prepared⁴⁰ by the addition of 2.0 g. of N-methyl-N-nitroso-N'-nitroguanidine to a solution containing 6 ml. of 50% potassium hydroxide and 40 ml. of ether, followed by distillation into a flask cooled in a Dry Ice bath). The ether was allowed to evaporate and the resulting oil was separated by vapor phase chromatography. The product mixture was separated into two components which were collected and analyzed by infrared and nuclear magnetic resonance spectroscopy.

The infrared spectrum of the second component was found to be identical with the authentic sample of 4,4-dimethylheptan-6-on-1-oic acid methyl ester synthesized as described above, as was its retention time on a 10-ft. Carbowax column in a vapor phase chromatograph. The nuclear magnetic resonance spectrum was comparable, but because of poor resolution could not be compared exactly.

The first component had an infrared spectrum similar to the one described above, but it differed in the fingerprint region. The nuclear magnetic resonance spectrum was essentially identical with that obtained above; however, there was a 5-min. difference in retention time at 150° on a 10-ft. Carbowax column in a vapor phase chromatograph. The first component was therefore identified as 2,2-dimethylheptan-6-on-1-oic acid methyl ester.

Anal. Calcd. for C₁₀H₁₈O₂: C, 64.49; H, 9.74. Found: C, 63.80; H, 9.92.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVEY MUDD COLLEGE, CLAREMONT, CALIFORNIA]

Carbonium Ion Salts. VII. Synthesis of Tropenium Chloroborate and Related Reactions^{1,2}

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This paper reports the synthesis of tropenium chloroborate and the characterization of triphenylcarbonium chloroborate as easily preparable, reasonably stable salts of the BCl₄⁻ anion. Some reactions of boron chloride, boron bromide, and stannic chloride with organic hydride donors are discussed which show that carbon-to-metal halide hydride transfer is the source of carbonium ions in certain metal halide-hydrocarbon reactions.

There has been considerable interest in compounds containing the tetrachloroborate anion⁴; however, with the exception of Lappert's^{4c} synthesis of pyridinium chloroborate from pyridinium chloride and boron chloride in methylene chloride, the routes to simple chloroborate salts have involved high temperatures and pressures,^{4d} long milling of solids,^{4h} or liquid hydrogen chloride solvent,^{4g} and the products often give unsatisfactory analyses. Muettterties⁴ⁱ reports the preparation of cesium chloroborate by reaction of cesium chloride and boron chloride in a nitrobenzene slurry but finds that stoichiometric material is best prepared by use of a stainless steel pressure reaction vessel.

We find that the reaction of boron chloride with cycloheptatriene in methylene chloride solvent at room temperature proceeds smoothly to give tropenium chloroborate of high purity. The reaction is not accompanied by any observed decomposition of cycloheptatriene, and the crystalline product is isolated by removal of mother liquor with a pipet, washing with solvent, and drying *in vacuo*. Tropenium chloroborate prepared in this manner consists of transparent single needles, m.p. 119°. These crystals are not particularly hygroscopic,

but become coated with an opaque coat of boric acid on exposure to the atmosphere. The chloroborate dissolves slowly in cold water to give water-white solutions of tropenium ion, boric acid, and hydrogen chloride. The crystals can be kept for a long time in a dry atmosphere without any apparent change; the compound does not appear to be light sensitive like tropenium chloride or hydrogen dichloride.⁵

Tropenium chloroborate can also be prepared by reaction of boron chloride with cycloheptatriene in cyclohexane or by mixing the reactants neat, but the products are not as satisfactory. Reaction of tropenium chloride with boron chloride in methylene chloride affords tropenium chloroborate of good quality and confirms the ionic nature of the compound, but the difficulties inherent in the handling of tropenium chloride⁵ obviate this as a useful route to the chloroborate. Addition of *t*-butyl chloride to the reaction of cycloheptatriene and boron chloride in methylene chloride increases the yield, but the crystal size and quality of the product are not quite as good as in the reaction without *t*-butyl chloride cocatalyst.

Wiberg⁶ has reported a complex of boron chloride with triphenylmethyl chloride with correct analyses for (C₆H₅)₃CCl₂·BCl₃; this material is stable to 200°. We find that addition of boron chloride to a colorless solution of triphenylmethyl chloride in methylene chloride gives a deep red solution from which the 1:1 adduct is precipitated by cyclohexane as a yellow crystalline solid. In methylene chloride solvent this compound undergoes instantaneous hydride transfer with cycloheptatriene to give tropenium chloroborate and triphenylmethane; the material is thus an ionic salt⁷ and contains the BCl₄⁻

(1) Supported by the Petroleum Research Fund and the National Science Foundation.

(2) Reported in preliminary form in a communication: K. M. Harmon, A. B. Harmon, and F. E. Cummings, *J. Am. Chem. Soc.*, **83**, 3912 (1961).

(3) American Chemical Society, Petroleum Research Fund Scholar, 1960; National Science Foundation Scholar, 1961, 1962.

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