A Stereochemical Study of Product Formation from Some 4-*tert*-Butylcyclohexyl Cations[1]

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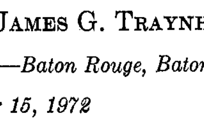
To assess the preferred stereochemistry of product formation from cyclohexyl carbonium ions, we have investigated the ratio of cis and trans products formed from several 4-*tert*-butylcyclohexyl systems. The reactions included lead tetraacetate and anodic oxidative decarboxylations of carboxylic acids, chlorinolyses of 2,4-dinitrobenzenesulfenates (products identified with both intimate and solvent-separated ion pairs), thermolyses of chlorocarbonates, and reactions of hydrogen chloride with tertiary alcohols and with olefins. Most carbonium ion processes with cyclohexyl systems, even those which involve solvent-separated ion pairs, are so strongly influenced by the stereochemistry of the reactant that they offer little information about the preferred stereochemistry of product formation from cyclohexyl cations. Secondary carbonium ions generated by lead tetraacetate oxidative decarboxylation and tertiary ones derived from alcohols, however, are apparently free so far as the stereochemical influence of the leaving group is concerned. For cyclohexyl cationic reactions in which the stereochemistry of the leaving group is not influential, and in which there is substantial bond making in the transition state, the preferred reaction path will lead to axial bond formation. The predominance of axial products in these reactions can be rationalized on the basis of torsional interactions, which hinder equatorial-like attack on the intermediate carbonium ions.

Several studies have established that the less stable, axially substituted products are formed preferentially or exclusively from cyclohexyl radical intermediates.[3] Our attempt to compare these results with those reported for other trivalent carbon intermediates was thwarted. Although there is a substantial volume of literature describing carbonium ion reactions of cyclohexyl systems, few of the papers illuminate the preferred stereochemistry of product formation from cyclohexyl cations.[4] Several cationic reactions involving cyclohexyl systems have been reported,[5] but in all of them the stereochemistry of the major products is directly tied to that of the reactant, even when the intervention of cationic intermediates is revealed by the 1,2-hydride shifts which occur.[5b] In order for the stereochemistry of product formation from cyclohexyl cations to be revealed, the counterion must be far enough removed so that it does not influence the direction of attack on the cation. Evidence of such a free carbonium ion[6] would be the formation of identical product mixtures from isomeric axial and equatorial reactants. In the present study, the preferred stereochemical paths of product formation from a number of different cyclohexyl cation precursors have been determined and compared.



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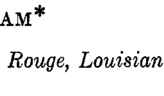

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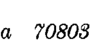

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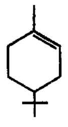

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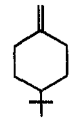

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In our study, we have used 4-*tert*-butylcyclohexyl systems and reactions which are expected to involve cyclohexyl cations. We have assumed that the cyclohexane rings are in the chair conformation and that the *tert*-butyl substituent (bulkiest substituent used) is always equatorial.[5a] Carbonium ion like reactions were effected by lead tetraacetate and anodic oxidations of carboxylic acids (Ia-COOH and Ie-COOH),[8] thermolyses of chlorocarbonates (Ia-OCOCl and Ie-OCOCl), chlorinolyses of 2,4-dinitrobenzenesulfenates (Ia-OSAr and Ie-OSAr), chlorodehydroxylations of tertiary alcohols (IIIa-OH and IIIe-OH), and additions of anhydrous hydrogen chloride to the isomeric olefins IV and V. The results are summarized in Table I. Of the systems which lead to secondary cyclohexyl cations, only the lead tetraacetate oxidations of Ia-COOH and Ie-COOH yielded identical product mixtures from the stereoisomeric reactants. In that reaction, the products consist of olefin and alkyl acetate, and axial acetate (Ia-OAc) is slightly favored over equatorial acetate (Ie-OAc). The chlorodehydroxylations of

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(1) (a) Based on the Ph.D. dissertation of S. D. E., Louisiana State University—Baton Rouge, Jan 1971. Grateful acknowledgment is made to the Dr. Charles E. Coates Memorial Fund of the LSU Foundation donated by George H. Coates for financial aid toward the preparation of that dissertation. (b) Presented in part at the Combined Southeast–Southwest Regional Meeting of the American Chemical Society, New Orleans, La., Dec 2, 1970, Paper ORGN 340. (c) A brief summary of a portion of these data has been published: S. D. Elakovich and J. G. Traynham, *Tetrahedron Lett.*, 1435 (1971).

(2) National Aeronautics and Space Administration Trainee, 1966–1969.

(3) (a) F. R. Jensen, L. H. Gale, and J. E. Rodgers, *J. Amer. Chem. Soc.*, **90**, 5793 (1968), and references cited therein; (b) J. G. Traynham, A. G. Lane, and N. S. Bhacca, *J. Org. Chem.*, **34**, 1302 (1969).

(4) Some discussions of the nomenclature of carbonium ions, in this journal and elsewhere, have been misleading because of the authors' failure to appreciate the distinction between one-word and two-word names. *Cyclohexyl carbonium ion* and *cyclohexyl cation* are both correct names for the same ion, and both (particularly the *cation* name) are preferred by us to *cyclohexenium ion* [G. A. Olah, *J. Amer. Chem. Soc.*, **94**, 808 (1972)], which is not formed in accord with usual IUPAC practice and emphasis. For a clear, definitive discussion of this matter, see C. D. Hurd, *J. Chem. Educ.*, **48**, 490 (1971).

(5) (a) S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955); (b) N. C. G. Campbell, D. M. Muir, R. R. Hill, J. H. Parish, R. M. Southam, and M. C. Whiting, *J. Chem. Soc. B*, 355 (1968); (c) D. S. Noyce, B. E. Johnson, and B. Weinstein, *J. Org. Chem.*, **34**, 463 (1969); (d) J. B. Lambert, G. J. Putz, and C. E. Mixan, *J. Amer. Chem. Soc.*, **94**, 5132 (1972); (e) J. E. Nordlander and T. J. McCrary, Jr., *ibid.*, **94**, 5133 (1972); (f) A. Streitwieser, Jr., and C. E. Coverdale, *ibid.*, **81**, 4275 (1959); (g) W. Hückel and K. Heyder, *Chem. Ber.*, **96**, 220 (1963).

(6) By "free," we refer only to the influence of the leaving group, not to association with solvent. Our discussion and data do not bear on the important nucleophilic role of solvent in the ionization process.[7]

(7) For a review, see D. J. Raber and J. M. Harris, *J. Chem. Educ.*, **49**, 60 (1972).

(8) In formula designations such as these, a and e will signify axial and equatorial bonding, respectively, of the functional group specified. The Roman numeral designates the substituted cyclohexyl group according to the illustrations in the text, and X is an unspecified functional group (not necessarily the same in all cases).

TABLE I

SUMMARY OF REACTIONS WITH 4-*tert*-BUTYLCYCLOHEXYL SYSTEMS

Reactant[a]	Reaction[d]	Substitution products[e]	% Axial product
Ia-COOH	$Pb(OAc)_4$, HOAc	I-OAc	53
Ie-COOH		I-OAc	53
Ia-COOH	$Pb(OAc)_4$, LiCl[f]	I-Cl	67
Ie-COOH		I-Cl	67
Ia-COOH	Anodic oxidation	I-OH	46
Ie-COOH		I-OH	30
Ia-OSAr[c]	Cl_2, HOAc	I-Cl (7.0)	36
		I-OAc (5.7)	19
		II-OAc (9.0)	83
Ia-OSAr[c]	Cl_2, HOAc, $LiClO_4$	I-Cl (<1)	<50
		I-OAc (5.6)	29
		II-OAc (8.7)	83
Ie-OSAr	Cl_2, HOAc	I-Cl (35)	57
		I-OAc (43)	33
		II-OAc (0.5)	100
Ie-OSAr	Cl_2, HOAc, $LiClO_4$	I-Cl (16.5)	62
		I-OAc (33)	48
		II-OAc (1.8)	100
Ia-OCOCl	Thermolysis	I-Cl	63
Ie-OCOCl		I-Cl	21
IIIa-OH	HCl	III-Cl	80
IIIe-OH		III-Cl	80
IV	HCl	III-Cl	65
V	HCl	III-Cl	70
Ia-OTs[b,c]	HOAc, 100°	I-OAc (8.1)	9
	0.05 *M* NaOAc	II-OAc (4.8)	94
Ie-OTs[b,c]	HOAc, 100°	I-OAc (19.9)	98
	0.05 *M* NaOAc	II-OAc (2.0)	25
Ia-OSO_2Me[b,c]	HOAc, 70°	I-OAc (9.3)	13
	0.1 *M* NaOAc	II-OAc (5.0)	92
Ie-OSO_2Me[b,c]	HOAc, 70°	I-OAc (20.9)	95
	0.1 *M* NaOAc	II-OAc (1.4)	21
Ia-NH_2[b,c]	H_2O, HONO	I-OH	44
Ie-NH_2[b]	H_2O, HONO	I-OH	14

[a] See ref 8. [b] From the literature (I-OTs,[5b] I-OSO_2Me,[5c] and I-NH_2[5g]). [c] More than 65 mol % of product mixture was olefin. [d] All reactions except one presumably involve carbonium ion intermediates. [e] Numbers in parentheses represent yield of product obtained in reactions by which multiple substitution products were produced. [f] Product formation from radical intermediate.

IIIa-OH and IIIe-OH also gave product mixtures (alkyl chlorides) indistinguishable from each other, with axial product predominating 4:1. The predominance of axial products in these two systems, as well as in the hydrochlorination of the olefins IV and V, is explained on the basis of torsional strain in the transition state, which hinders equatorial-like attack on the intermediate cation.[3a] The differences in the product mixtures from the other systems investigated indicate the difficulty of generating a cyclohexyl cationic center free from the influence of the leaving group.

Results

Oxidations of I-COOH.—Hydrogenation of 4-*tert*-butylbenzoic acid over platinum oxide catalyst produced a mixture of *cis*- and *trans*-4-*tert*-butylcyclohexanecarboxylic acids, which were separated by the use of thiourea.[9] Separate **lead tetraacetate oxidative decarboxylations**, carried out at 80° in benzene containing pyridine, converted the acids to a mixture of olefin and alkyl acetates (Ia-OAc and Ie-OAc) through alkyl cation intermediates.[10] The product mixtures were analyzed by comparison of gas chromatographic (gc) and nuclear magnetic resonance (nmr) data with those of authentic samples. The same proportions of Ia-OAc and Ie-OAc (53:47, respectively) were obtained from both stereoisomeric carboxylic acids. The yields of olefin (30 and 38%) were not the same from the two isomeric reactants, but they were both moderately low and contrast with the high ones (76–87%) obtained by acetolysis of 4-*tert*-butyl-1-cyclohexyl toluene- and methanesulfonates.[5b,c]

Since the alkyl cation intermediate in this reaction is presumably generated from an alkyl radical,[10b] the stereochemistry of product formation from this radical precursor is of immediate interest and concern. The halodecarboxylation of a carboxylic acid by use of lead tetraacetate and lithium halide provides an alkyl halide formed from an alkyl radical which is generated under conditions which are quite similar to those for the cationic oxidative decarboxylations.[11] Separate halodecarboxylations of Ia-COOH and Ie-COOH by lead tetraacetate in the presence of lithium chloride give alkyl chloride mixtures indistinguishable from each other, with axial chloride (Ia-Cl) predominating 2:1.[12a] The thermal decompositions of the tertiary hypochlorites, Ia-$C(CH_3)_2OCl$ and Ie-$C(CH_3)_2OCl$, give this same 2:1 cis:trans chloride product ratio,[12b] indicating that the same type of radical intermediate is formed in both reactions. Since in the halodecarboxylation reaction the same radical is formed from both acids, it follows that the oxidation of this radical would lead to a single type of carbonium ion intermediate. Therefore, both the radical and the cationic lead tetraacetate reactions are independent of the configuration of the starting acid (so far as product stereochemistry is concerned), but product formation from the apparently free cationic intermediate is appreciably less stereoselective than it is from the apparently free radical from which the cation is formed.[13]

Recent studies of **anodic oxidations** of carboxylic acids identify the ester, alcohol, and olefin products with cationic intermediates.[14] Although a combination of radical and cationic processes may be involved in the formation of these products in aqueous solutions,

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[9] H. van Bakkum, P. E. Verkode, and B. M. Wepster, *Kon. Ned. Akad. Wentensch. Proc., Ser. B*, **62**, No. 3 (1959); *Chem. Abstr.*, **54**, 2209*f* (1960).

[10] (a) E. J. Corey and J. Casanova, Jr., *J. Amer. Chem. Soc.*, **85**, 165 (1963); (b) J. K. Kochi, *ibid.*, **87**, 1811 (1965).

[11] J. K. Kochi, *ibid.*, **87**, 2500 (1965); *J. Org. Chem.*, **30**, 3265 (1965).

[12] (a) Since the completion of our study, the same results for these reactions have been reported by R. D. Stolow and T. W. Giants, *Tetrahedron Lett.*, 695 (1971); (b) F. D. Greene, C.-C. Chu, and J. Walia, *J. Amer. Chem. Soc.*, **84**, 2463 (1962).

[13] A referee has suggested that the identity of the product mixtures from the isomeric acids may "indicate no more than conformational equilibration of counterspecies at some point prior to product formation." Even this point of view does not reduce the stereochemical significance of our results, however. Because the configurational compositions of the radical and cationic product mixtures are quite different from one another, the cationic result cannot be dictated directly by the radical one, and configurational preferences of cation–counterion pairs would be as independent of those of precursor species as would those of free carbonium ions. Whether one advocates a free carbonium ion[6] or an ion pair intermediate, the ratio of acetate products (53 axial:47 equatorial) demonstrates that there is little configurational preference at this cationic stage and the configuration of the original reactant has no influence. The results which we have obtained with the tertiary alcohols IIIa-OH and IIIe-OH lead us to favor the free carbonium ion[8] interpretation.

[14] For example, see (a) E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova, Jr., and E. T. Kaiser, *J. Amer. Chem. Soc.*, **82**, 2645 (1960); (b) W. H. Koehl, Jr., *ibid.*, **86**, 4686 (1964); (c) J. G. Traynham and J. S. Dehn, *ibid.*, **89**, 3129 (1967); (d) J. G. Traynham, E. E. Green, and R. F. Frye, *J. Org. Chem.*, **35**, 3611 (1970), and references cited therein.

TABLE II

PRODUCT DISTRIBUTIONS[a] FROM THE CHLORINOLYSIS IN ACETIC ACID OF *cis*- AND *trans*-4-*tert*-BUTYLCYCLOHEXYL 2,4-DINITROBENZENESULFENATES

Sulfenate	Ia-Cl	Ie-Cl	Ia-OAc	Ie-OAc	IIa-OAc	IIe-OAc	Olefin[b]	$\frac{\text{R-OAc}}{\text{R-Cl}}$
Ie-OSAr	20	15	14	29	0.5		22	1.2
Ie-OSAr ($LiClO_4$)	10	6.2	16	17	1.8		48.5	2.1
Ia-OSAr	2.5	4.5	1.1	4.6	7.5	1.5	78	2.1
Ia-OSAr ($LiClO_4$)	<0.5	<0.5	1.6	4.0	7.2	1.5	85	>15

[a] Figures represent an average of two runs which gave numbers differing from the average by no more than 3% of the average figure. [b] Detected as the addition product mixture formed by reaction of 4-*tert*-butylcyclohexene and chlorine in acetic acid solvent (See Experimental Section for details).

the major portions of alcohol and olefin products appear to come from cationic intermediates,[14d] which are considered to be higher in energy than those generated by solvolysis reactions.

We have electrolyzed 0.5 *M* aqueous solutions of Ia-COONa and Ie-COONa at graphite anodes. The conversion was quite low for both isomers, and yields were not calculated. The product mixtures were complex, and only the stereochemical ratios of the major components, the *cis*- and *trans*-4-*tert*-butylcyclohexanols, were examined. While Ie-OH is the predominant product from both acids, its predominance in the mixture from Ie-COOH is substantially greater than it is from Ia-COOH. The intermediate carbonium ions in these electrolyses are generated from alkyl radicals absorbed on the anodic surface, and we were surprised that the configuration of the starting acid influences the final product-forming step. Apparently the departure of the freshly formed carbonium ion from the anodic surface is not so much in advance of its combination with solvent water that the surface has no effect on the regioselectivity of alcohol production.

Chlorinolysis of Arenesulfenates.—The most widely accepted description of carbonium ion reactions is that of Winstein and coworkers.[15] It includes different kinds of ionic intermediates, any or all of which may form products. The extent and nature of the solvent

$$\begin{array}{ccccccc} RX & \rightleftharpoons & R^+X^- & \rightleftharpoons & R^+||X^- & \rightleftharpoons & R^+ + X^- \\ & & \text{intimate} & & \text{solvent-} & & \text{dissociated} \\ & & \text{ion pair} & & \text{separated} & & \text{ions} \\ & & & & \text{ion pair} & & \end{array}$$

environment of a carbonium ion strongly influences the stereochemical behavior of that ion. The ion-pairing behavior of the intermediates involved in the chlorinolysis in acetic acid of alkyl 2,4-dinitrobenzenesulfenates has been extensively characterized by means of the lithium perchlorate effect criterion.[16] Generally, the arenesulfenate is chlorinated to form an intimate sulfoxonium ion pair, which may lose a sulfinyl chloride fragment, before or after solvent reorganization, to form the corresponding carbonium ion pair. These carbonium ion pairs are "born in an inherited solvent environment;"[16a] that is, the solvent structure organized about the intimate and solvent-separated sulfoxonium ion pairs is transferred to the corresponding carbonium ion pairs, which do not interconvert.[16b,c] The effect of lithium perchlorate on the product mixtures of systems studied has led to the conclusion that acetate products arise principally from solvent-separated carbonium ion pairs and chloride products from intimate carbonium ion pairs.[16b] Thus, the stereochemistry of product formation from both kinds of ion pairs is subject to investigation.

Isomerically pure *cis*- and *trans*-4-*tert*-butylcyclohexyl 2,4-dinitrobenzenesulfenates were prepared from the isomerically pure alcohols[17] and freshly recrystallized 2,4-dinitrobenzenesulfenyl chloride. Chlorinolysis in acetic acid of each sulfenate was effected at 20° with a 2:1 molar ratio of chlorine to sulfenate, both without and with added lithium perchlorate. The products were identified by comparison of their gc retention times with those of authentic samples, and the yield of each product was calculated from the gc data and the relative response factor for that component. The results are summarized in Tables I and II.

Chlorinolysis of the trans sulfenate, Ie-OSAr, gives predominantly 4-*tert*-butylcyclohexyl acetate; 4-*tert*-butylcyclohexene and 4-*tert*-butylcyclohexyl chloride are formed in lesser amounts. In the presence of lithium perchlorate, the olefin becomes the predominant product. Although the absolute amount of acetate decreases, the ratio of acetate to chloride increases almost twofold; thus, the olefin is formed at greater expense of the chloride than of the acetate. This unequal effect of lithium perchlorate on the acetate and chloride products indicates that substantial amounts of these products arise from different intermediates. Earlier workers[16] have shown for other alkyl systems that chloride product comes predominantly or exclusively from intimate ion pairs and acetate and olefin products come from other intermediates. The decrease in yield of acetate with added lithium perchlorate in the present system (an effect not reported for previously studied systems) indicates either that a substantial amount of the acetate must arise from intimate ion pairs or that, with lithium perchlorate present, another ionic intermediate (*e.g.*, completely separated ions) becomes inportant and gives rise to acetate and olefin in different proportions than do the solvent-separated ion pairs.[18] The latter interpretation is the more consistent with

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(15) S. Winstein, P. E. Klinedinst, Jr., and G. C. Robinson, *J. Amer. Chem. Soc.*, **83**, 885 (1961).

(16) (a) H. Kwart and J. L. Irvine, *ibid.*, **91**, 5541 (1969); (b) H. Kwart, E. N. Givens, and C. J. Collins, *ibid.*, **91**, 5532 (1969); (c) J. G. Traynham and A. W. Foster, *ibid.*, **93**, 6216 (1971).

(17) An initial attempt to prepare isomerically pure *cis*- and *trans*-4-*tert*-butylcyclohexanols by the fractional crystallization of their phthalate derivatives[6a] proved tedious. Spinning-band distillation of the corresponding acetates, followed by hydrolysis, gave a convenient pathway to large amounts of the isomerically pure alcohols.

(18) Independent studies (H. Kwart and J. W. Boghosian, private communications, 1971) of this system have shown that added lithium chloride has little effect on the product distributions from I-OSAr without lithium perchlorate present but has a substantial effect on those from I-OSAr with lithium perchlorate present. These results strongly imply that completely separated ions are important in the reaction sequence when lithium perchlorate is present but unimportant when it is absent.

all other data reported for chlorinolyses of sulfenates.[16,18] The great increase in proportion of olefin when lithium perchlorate is included in the reaction mixture suggests that olefin is formed mainly from intermediates other than intimate ion pairs.

Chlorinolysis of the cis sulfenate, Ia-OSAr, yields predominantly 4-*tert*-butylcyclohexene, both in the presence and in the absence of lithium perchlorate. This result is harmonious with those obtained for other systems having axial reactant groups. The nitrous acid deamination of *cis*-4-*tert*-butylcyclohexylamine also gives olefin in high yield;[5g] in fact, axial cyclohexylamines generally give high yields of olefin.[19a] The solvolysis of each 4-*tert*-butylcyclohexyl arene- or methanesulfonate gives predominantly elimination rather than substitution product, but the axial sulfonates give about 10% more olefin than do the equatorial sulfonates.[5b,c] The stereochemistry of an axial substituent normally favors elimination over substitution, probably because the solvating molecule equatorially associated with the developing carbonium ion center is favorably located to assist in the removal of the vicinal axial hydrogen. (An axially associated solvent molecule is not so located.)

The effect of lithium perchlorate on the chloride: acetate product ratio from the cis sulfenate (Ia-OSAr) is dramatic. The chloride yield is reduced by a factor of >6, while the yield of acetate is only slightly reduced. This effect strongly implies that the chlorides are intimate ion pair products, and that the acetate must arise predominantly from solvent-separated ion pairs. The increase in olefin with lithium perchlorate addition implies that olefin is also a product of solvent-separated ion pairs.

Although lithium perchlorate addition reduces the absolute amount of chloride products from both Ia-OSAr and Ie-OSAr, the isomeric distribution from each reactant remains unchanged, supporting the conclusion that the chlorides are formed only from intimate ion pairs. Since the stereochemistry of each chloride mixture is directly related to that of the sulfenate from which it is obtained (36–43% retention, 64–57% inversion[20]), these results are of little value in elucidating the preferred stereochemistry of product formation from cyclohexyl cations.

Predominant inversion could be taken to imply a substantial amount of SN2-like displacement by chloride on the $ROS(Cl)Ar^+$ ion, but the extensive amount of retention requires another process as well. It seems unlikely to us that partitioning between SN2 and ionizing processes leading to RCl would be about the same with both axial and equatorial reactants. The orientation between cation and chloride in the intimate ion pair is not inflexible; transannular rearrangement is as extensive in the chloride product as in the acetate one from cyclooctyl arenesulfenate.[16c] Therefore both retention and inversion could occur in the RCl formation from carbonium chloride intimate ion pairs.

Four isomeric acetates are formed in the chlorinolysis reactions: *cis*- and *trans*-4-*tert*-butylcyclohexyl acetate (Ia-OAc and Ie-OAc) and *cis*- and *trans*-3-*tert*-butylcyclohexyl acetate (IIe-OAc and IIa-OAc). The trans sulfenate gives a very small amount of IIa-OAc, whereas this is the major acetate from the cis sulfenate. Both rearrangement (1,2-hydride shift) and elimination processes are more extensive with the cis sulfenate than with the trans sulfenate.

Substantial amounts of hydride-shift products are also obtained from solvolysis of cyclohexyl arenesulfonates, usually more so from axial than from equatorial reactants.[5a–e] These products have led to the suggestion that one or more hydrogen-bridged species intervene.[5a,b] Such species conveniently account for the preferred formation of IIa-X[21] and for the formation of large amounts of olefin from Ia-X. Alternatively, a twist–boat conformation for the rearranged ion may be the important precursor to IIa-OAc,[18] since a single hydrogen-bridged species will not account for the preferred axial stereochemistry of II-OAc from both isomers of I-OSAr. The absence of rearranged chloride products in the sulfenate product mixtures implies that hydrogen bridging is unimportant in the intimate ion pairs in this system and contrasts sharply with data from the cyclooctyl system.[16c] Although the extents of transannular hydride shifts are the same in the intimate and solvent-separated carbonium ion pairs generated by chlorinolysis of cyclooctyl arenesulfenate,[16c] 1,2-hydride shift occurs far more extensively in the separated ion pairs of the cyclohexyl system than in the intimate ones.

The difference in the ratio of stereoisomers of I-Cl and of I-OAc and the insignificant effect of lithium perchlorate on the distribution of the isomeric acetates derived from cis sulfenate together demonstrate that little, if any, of these acetates is formed from intimate ion pairs. In contrast to these results with cis sulfenate, lithium perchlorate does bring about a significant change in the Ie-OAc:Ia-OAc ratio (from about 2:1 to about 1:1) obtained from trans sulfenate. This change, coupled with the accompanying reduction in yield of acetate, strongly implies that, with lithium perchlorate present, a substantial portion of the acetate-forming process from trans sulfenate is shifted from solvent-separated ion pairs to completely separated ions.[18] The chloride product is formed mainly with inversion of configuration from each sulfenate, but the ionic intermediates derived from cis sulfenate and from trans sulfenate exhibit different stereochemistry of formation of acetate products. Those from cis sulfenate (with or without added lithium perchlorate) form equatorial acetate (inverted configuration) preferentially (4:1), those from trans sulfenate without added lithium perchlorate also form equatorial acetate (retention of configuration) preferentially (2:1); but those from trans sulfenate with added lithium perchlorate form axial and equatorial products in an approximately 1:1 ratio, just as we observed in the lead tetraacetate oxidation of Ie-COOH and Ia-COOH. These results reveal that carbonium ions free from the stereochemical influence of the leaving group (or other associated

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(19) (a) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., pp 89–91; (b) pp 99–100.

(20) The yield of chloride from Ia-OSAr with added lithium perchlorate was too small for us to determine the cis:trans chloride ratio accurately, but the inverted chloride was clearly the major isomer.

(21) Covalent return from the rearranged ion pair intermediates generated from substituted cyclohexyl tosylates has been suggested to account for the predominant stereochemistry of the ultimate products;[5b,e] for example, axial tosylate rearranges mainly to equatorial tosylate, which gives axial acetate. A parallel process, however, for the carbonium acetate ion pairs generated from arenesulfenates would produce mainly equatorial acetate (IIe-OAc) from axial sulfenate, while the actual result is mainly axial acetate (IIa-OAc).

anion) are seldom, if ever, involved in these sulfenate reactions. We have speculated about a variety of competing product-forming processes, each with its own stereochemical consequences, occurring with the several ionic intermediates. Our data do not, we believe, permit us to make firm choices to account exactly for the observed stereochemical results.

We investigated brominolysis of the arenesulfenates, Ia-OSAr and Ie-OSAr, using the same procedure as we did for chlorinolysis. No monobromides were present in the product mixtures, I-OAc was the major product, and it was formed with about 96% retention of configuration from each sulfenate. Addition of lithium perchlorate to the initial reaction mixtures increased slightly the yields of both olefin and rearranged acetate (II-OAc) products at the expense of the major acetate product, but the changes were not extensive enough to be the basis for meaningful interpretations. The data do imply that intimate ion pairs are far less important for product formation in brominolysis than in chlorinolysis of the arenesulfenates.

Thermolysis of Chlorocarbonates.—The rate-determining step in the thermal decomposition of chlorocarbonates appears to involve a carbonium ion,[22] but the nature of this ion has not been fully defined. The decomposition has recently been described by an ion pair mechanism.[23] We thought it of interest to compare the stereochemistry of product formation from this reaction with that observed from the different kinds of ion pairs in the arenesulfenate chlorinolysis. Thermal decomposition of both *cis*- and *trans*-4-*tert*-butylcyclohexyl chlorocarbonates, obtained from the reaction of phosgene with the isomeric 4-*tert*-butylcyclohexanols, yields as the major chloride product the isomer with retained configuration. This result suggests an SNi mechanism for the decomposition. However, since chloride with retained configuration is only the predominant and not the exclusive product, an unmodified SNi process can account only for the major part of the reaction mixture. It is clear that if an ion-pair mechanism is involved in this reaction, the ion pairs are different from both the intimate and the solvent-separated ion pairs of the sulfenate chlorinolysis reaction.

Tertiary Carbonium Ions.—We have compared some reactions of tertiary cyclohexyl cations with the reactions of secondary ones described above. We have used acidic conditions with both tertiary alcohols and olefins to generate the tertiary carbonium ions.

A 1:1 ratio of the *cis*- and *trans*-1-methyl-4-*tert*-butylcyclohexanols, obtained from a Grignard reaction of 4-*tert*-butylcyclohexanone, was converted to a mixture of the isomeric acetates, which were separated by spinning band distillation and then hydrolyzed to the isomerically pure alcohols. Anhydrous hydrogen chloride reacted with each alcohol to give chloride products, III-Cl, arising from a tertiary carbonium ion. Identical product mixtures, rich in axial chloride (80%), were obtained from both isomers. The chlorides were identified by their nmr spectra (see Experimental Section for details). Hydrochlorination of the olefins IV and V would presumably go through the same tertiary cyclohexyl cation as is produced from the alcohols. Addition of hydrogen chloride gas to a methylene chloride solution of IV gave III-Cl as the only products, with an axial:equatorial chloride ratio of 65:35.[24] A similar treatment of V gave 70% axial chloride and 30% equatorial chloride as the only products. The high preference for attack which results in axial bond formation can be explained by torsional interactions, as has been done for the same preference in attack on cyclohexyl radicals.[3a] Attack on the essentially planar cationic center from a direction leading to equatorial bond formation will increase torsional interaction, since the methyl group (on C-1) must eclipse the equatorial hydrogens on C-2 and C-6 at some stage in the reaction; no such interaction would occur with attack leading to axial bond formation. To the degree that bond formation is substantial at the transition state, the rate of axial attack will exceed that of equatorial attack. If hydrogen rather than methyl is on C-1, the torsional interaction should be much smaller, and therefore, the preference for axial product formation should be much less. This expectation corresponds exactly to the observation in the case of lead tetraacetate oxidative decarboxylation (change in a-X:e-X from 80:20 for III-Cl from III-OH to 53:47 for I-OAc from I-COOH).

In a previous investigation of the chlorodehydroxylation of mixtures of IIIa-OH and IIIe-OH, the ratio of IIIa-Cl:IIIe-Cl was found to be 5.9:1.[26] The stereochemical assignments were made on the basis of the infrared spectra of the products and the selective dehydrochlorination of IIIa-Cl. We made our stereochemical assignments on the basis of the nmr line width of the methyl adsorption in each isomer (see Experimental Section for details). The axial methyl adsorption is broadened because of "W" coupling with the axial protons at the two adjacent ring positions.[27] The measured line-width values fall well within the predicted range for each isomer,[28] and the stereochemical assignments agree with those made on the basis of infrared data.[26]

Conclusions

Most carbonium ion processes with cyclohexyl systems, even those which involve solvent-separated ion

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[22] (a) K. B. Wiberg and T. M. Shryne, *J. Amer. Chem. Soc.*, **77**, 2774 (1955); (b) K. L. Oliver and W. G. Young, *ibid.*, **81**, 5811 (1959).

[23] J. L. Kice and G. C. Hanson, *Tetrahedron Lett.*, 2927 (1970).

[24] The axial chloride might have been expected to be the major product from the hydrochlorination of IV, since most additions to double bonds proceed by a diaxial pathway,[19b] but deuterium chloride reacts with 3-methyl-2-cholestene to give the diequatorial adduct.[25]

[25] (a) D. H. R. Barton, A. da S. Campos-Neves, and R. C. Cookson, *J. Chem. Soc.*, 3500 (1956); (b) D. H. R. Barton, *Experientia, Suppl.*, II, 121 (1955).

[26] N. L. Allinger and C. D. Liang, *J. Org. Chem.*, **32**, 2391 (1967).

[27] (a) C. W. Shoppee, F. P. Johnson, R. E. Lack, J. S. Shannon, and S. Sternhell, *Tetrahedron, Suppl.*, **8**, Part II, 421 (1966). (b) The minor isomer, IIIe-Cl, is difficult to obtain completely free of IIIa-Cl by preparative gc, apparently because of some isomerization on the metal surfaces of the splitter or exit port. The chemical shifts of CH_3CCl in the two isomers are so close together that contamination of IIIe-Cl by IIIa-Cl raised some doubts about the dependability of the differentiation based on nmr line widths. After extensive experimentation in these laboratories, Dr. E. E. Green confirmed our nmr differentiation of the isomers. Dr. Green also found that the compositions of various mixtures of IIIa-Cl and IIIe-Cl were not changed by heating at 110° in sealed glass ampoules, with and without solvent, with and without added hydrogen chloride. These experiments strongly support our view, implied in the discussion, that the isomer mixture obtained results from kinetic rather than thermodynamic control, even though its composition is close to that of the equilibrium mixture.[26] We acknowledge with appreciation Dr. Green's contribution to this investigation.

[28] D. N. Kirk and P. M. Shaw, *J. Chem. Soc. C*, 182 (1970), found no difference in the line widths of the methyl adsorptions of the isomers IIIa-Cl and IIIe-Cl. These authors, apparently misinterpreting the nomenclature used by Allinger and Liang,[26] assign axial-Cl stereochemistry to the minor isomer.

pairs, are so strongly influenced by the stereochemistry of the reactant that they offer little information about the preferred stereochemistry of product formation from cyclohexyl cations. Secondary carbonium ions generated by lead tetraacetate oxidative decarboxylation and tertiary ones derived from alcohols, however, are apparently free so far as the stereochemical influence of the leaving group is concerned. For cyclohexyl cationic reactions in which the stereochemistry of the leaving group is not influential, and in which there is substantial bond making in the transition state, the preferred reaction path will lead to axial bond formation. The degree of preference is small for secondary cations, but substantial for tertiary ones.

Experimental Section

Nuclear magnetic resonance (nmr) spectra were obtained on a Varian Associates Model A-60A spectrometer unless otherwise stated. Carbon tetrachloride (CCl_4) and deuteriochloroform ($CDCl_3$) were normally used as solvents with tetramethylsilane as the internal standard. Gas chromatographic (gc) analyses were obtained with either a Beckman GC-5 or a Hewlett-Packard Model 700 gas chromatograph, each equipped with a flame ionization detector and 0.125-in. columns. Spinning-band distillations were carried out on a Nester/Faust Teflon annular spinning band column, Model NFT-50. Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are uncorrected. Element microanalyses were done by Mr. Ralph Seab of these laboratories.

Preparation of *cis*- and *trans*-4-*tert*-Butylcyclohexanecarboxylic Acids.—Hydrogenation of 30 g of 4-*tert*-butylbenzoic acid in 150 ml of acetic acid with 2 g of platinum oxide and 50 psig of hydrogen pressure was complete in 1 hr. The resulting isomeric mixture was separated by the use of thiourea, which preferentially entraps Ie-COOH when crystallized from methanol solution.[9] Isolated were Ie-COOH, mp 173.5–174.5° (lit.[9] mp 175–176°), and Ia-COOH, mp 116–117° (lit.[9] mp 118–118.5°).

Preparation of Ia-OH and Ie-OH.—A commercial mixture of Ia-OAc and Ie-OAc was conveniently separated by distillation through a spinning band column, and saponification of each acetate gave the isomerically pure alcohol. From the trans acetate[29] we obtained Ie-OH, mp 79–79.8° (lit.[5a] mp 81–82°), and from the cis acetate,[29] Ia-OH, mp 78–79° (lit.[5a] mp 80–81°).

Preparation of IIa-OAc and IIe-OAc.—4-*tert*-Butyl-1-cyclohexene[5a] [bp 50° (10 mm), nmr (CCl_4) δ 5.6 (m, 2, C=CH)], prepared by dehydration of a mixture of I-OH with thionyl chloride in refluxing benzene solution, was converted to a mixture of four alcohols in 70% yield by hydroboration.[30] A mixture of the alcohols (20.4 g), sodium acetate (20 g), and acetic anhydride (100 ml) was refluxed for 3 hr, cooled, poured into ice water, and extracted with ethyl ether. The ether solution was dried and concentrated. Gc analysis of the product residue on four different columns (9.5 ft Carbowax 20M, 6 ft UC-W98, and 9.25 and 12 ft XF-1150) showed four clearly separated peaks of approximately equal intensity.[31] By use of authentic samples, the second and fourth peaks were assigned to Ia-OAc and Ie-OAc, respectively. By distillation through a spinning-band column, the acetate mixture was substantially resolved into its four components. The component corresponding to the first gc peak gave an nmr spectrum ($DCCl_3$) indicative of IIa-OAc: δ 0.83 (s, *tert*-butyl), 2.05 (s, $OCOCH_3$), 0.8–2.1 (21 total, ring protons, *tert*-butyl, $OCOCH_3$ superimposed), 5.14 (1, CHOAc, shape indicative of equatorial H). The distillate corresponding to the third gc peak gave an nmr spectrum ($DCCl_3$) indicative of IIe-OAc: δ 0.83 (s, *tert*-butyl), 2.02 (s, $OCOCH_3$), ~4.65 (m, broad shape indicative of axial H, CHOAc).

Partial saponification of the mixture of four acetates with 0.5 molar equiv of sodium hydroxide in 95% ethanol confirmed the nmr stereochemical assignments. The third and fourth gc peaks were greatly diminished, relative to the first and second ones, by the partial hydrolysis. Equatorial acetates undergo hydrolysis more rapidly than do axial acetates,[29] and a control experiment with a mixture of Ia-OAc and Ie-OAc confirmed the expected difference in rates for this system.

TABLE III

SUMMARY OF **HCX** NMR CHEMICAL SHIFTS

	δ[a]	
Compd	Axial H	Equatorial H
I-OAc	4.52	4.95
	4.60[b]	5.01[b]
	4.53[c]	4.90[c]
	4.70[d]	5.09[d]
	4.70[e]	5.10[e]
I-OH	3.37	3.98
I-Cl	3.72	4.46
	3.75[b]	4.44[b]
I-Br	4.18	4.67
I-OSAr[f]	3.58	3.96
I-OCOCl	4.70	5.12
I-OSOCl	5.08	5.51
II-OAc	~4.65[b,g]	5.14[b]

[a] 60-MHz spectra, relative to internal TMS reference, 10% solutions, CCl_4 solvent except where indicated; axial H absorption broader than equatorial H absorption in all cases. [b] $DCCl_3$ solvent. [c] DMSO-d_6 solvent. [d] Pyridine solvent. [e] Benzene solvent. [f] Ar = 2,4-dinitrophenyl. [g] Some uncertainty in precise location because of overlapping absorptions by Ia-OAc present.

Lead Tetraacetate Oxidative Decarboxylation of Ia-COOH and Ie-COOH.—The method used is essentially that described by Corey and Casanova.[10a] All reactions were carried out under nitrogen in a flame-dried apparatus. In a typical experiment a solution of 5 g (0.03 mol) of cis acid, 2.8 g (0.035 mol) of dry pyridine, 100 ml of freshly distilled benzene, and 17.7 g (0.04 mol) of lead tetraacetate was refluxed for 8 hr. After work-up, gc analysis (10 ft Carbowax 20M column at 130°) of the products by comparison with authentic samples showed 38% (mol %) 4-*tert*-butylcyclohexene, 30% Ia-OAc, 27% Ie-OAc, and about 5% other products arising from Ia-COOH. Similar analysis of the products from Ie-COOH showed 30% (mol %) 4-*tert*-butylcyclohexene, 34% Ia-OAc, 29% Ie-OAc, and about 6% other products. The "other products" in both cases corresponded in retention times to Ia-OH, Ie-OH, IIa-OAc, and IIe-OAc, in approximately equal amounts. Nmr spectra (100 MHz) of the product mixtures supported the gc assignments, but the "other products" were not detected by nmr.

Halodecarboxylation of *cis*- and *trans*-4-*tert*-Butylcyclohexanecarboxylic Acids.[11]—The same mixture of Ia-Cl and Ie-Cl was isolated in 50–70% yield from a reaction mixture of either Ia-COOH or Ie-COOH (1.0 g, 5.4 mmol), dry benzene (10 ml), lead tetraacetate (2.4 g, 5.4 mmol), acetic acid (1.2 g, 19 mmol), and lithium chloride (0.23 g, 5.4 mmol) heated at 80° for 0.5 hr. Gc analysis did not reveal any other products, and the Ia-Cl:Ie-Cl gc ratio of 2:1 was confirmed by nmr data (relative intensities of the two CHCl absorptions).

Anodic Oxidations[14d] of Ia-COOH and Ie-COOH.—A large, flat-bottomed glass tube was fitted with a nitrogen inlet, thermometer, disc-shaped copper cathode, carbon anode, and stirring bar. The reaction temperature was regulated by a water bath. Current was supplied by a direct current power supply that allowed variation of the voltage applied across the electrolysis cell. In a typical experiment, 5.0 g (0.03 mol) of I-COOH, 1.2 g (0.03 mol) of sodium hydroxide, and 60 ml of water (for a 0.5 *M* solution) were placed in the electrolysis cell, and current was applied. The current flow was small and decreased with reaction time; heating the reaction mixture to 80° aided current flow in most cases. The electrolysis had to be interrupted repeatedly to remove a polymer-like material from the anode which impeded current flow. The aqueous solution was filtered to remove any carbon particles, made basic with sodium hydroxide, and extracted with ether. The ethereal extract was dried (magnesium sulfate) and concentrated. The residue was then subjected to gc analysis. The aqueous portion from the work-up was made acidic with hydrochloric acid to recover any unreacted I-COOH.

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(29) N. B. Chapman, R. E. Parker, and P. J. A. Smith, *J. Chem. Soc.*, 3634 (1960).

(30) H. C. Brown and M. K. Unni, *J. Amer. Chem. Soc.*, **90**, 2902 (1968).

(31) Gc analysis for the alcohol mixture on the Carbowax 20M and XF-1150 columns showed only two product peaks, and the nmr spectrum showed only three absorptions (CCl_4, δ 3.45, 4.0, and 4.1) easily assigned to **C**H**O**H.

Only small amounts of products were obtained; over 90% of the acid was recovered. The main products, identified from their gc retention times (9.5 ft Carbowax 20M and 9.25 ft XF-1150 gc columns at 160°) as Ia-OH and Ie-OH, were present in a 1.0:1.15 ratio in the mixture from Ia-COOH and in a 1.0:2.4 ratio in the one from Ie-COOH. There were several unidentified minor products.

Preparation of Ia-OSAr and Ie-OSAr.—The 2,4-dinitrobenzenesulfenates were prepared[16b] from equimolar amounts of freshly recrystallized 2,4-dinitrobenzenesulfenyl chloride, mp 96–98°, and Ia-OH or Ie-OH in ethylene chloride solution containing pyridine. The yield of bright yellow crystals was 50–60%. Prepared were Ie-OSAr [mp 143.5–146°; nmr (CCl_4) δ 0.8–2.5 (18, cyclohexane ring and *tert*-butyl), 3.58 (m, 1, CHOSAr), 8.0 (d, 1, J = 9 Hz, aromatic), 8.5 (dd, 1, J = 9 and 2.4 Hz, aromatic), 9.11 (d, 1, J = 2.4 Hz, aromatic). *Anal.* Calcd for $C_{16}H_{22}N_2O_5S$: C, 54.2; H, 6.3. Found: C, 54.2; H, 6.5.] and Ia-OSAr [mp 161.5–162°; nmr (CCl_4) δ 0.8–2.5 (18, cyclohexane ring and *tert*-butyl), 3.96 (m, 1, CHOSAr), 7.97 (d, 1, J = 9 Hz, aromatic), 8.5 (dd, 1, J = 9 and 2.4 Hz, aromatic), 9.13 (d, 1, J = 2.4 Hz, aromatic). *Anal.* Found: C, 54.3; H, 6.2.].

Chlorinations in Acetic Acid of Ia-OSAr and Ie-OSAr.—The reactions between chlorine and each of the 2,4-dinitrobenzenesulfenates in acetic acid solution were carried out according to the published procedure.[16a,b] A typical experiment utilized 84 ml of dry acetic acid (distilled from acetic anhydride), 2.0 g (5.7 mmol) of Ia-OSAr or Ie-OSAr, 0.49 ml (11 mmol) of chlorine, and, if lithium perchlorate were used, 0.5 g (4.7 mmol) of lithium perchlorate. After work-up and concentration of the pentane extract of the reaction mixture,[16a] the oil obtained in each experiment was subjected to gc analyses. Separation of all components at once was difficult, but of the columns used (9.5 ft 10% Carbowax 20M, 6 ft UC-W98, and 9.5 and 12 ft 5% XF-1150, at temperatures from 110 to 160°), the XF-1150 one proved to be the most satisfactory. The products were identified by comparison of gc and nmr data with those of authentic samples. A substantial portion of each mixture was a group of olefin addition products, which gave a gc trace identical with that obtained from the product mixture formed by the addition of chlorine to 4-*tert*-butylcyclohexene but was not otherwise identified. The small peaks for Ia-OH and Ie-OH overlapped other peaks in the gc trace but quantitative analysis was effected by silylation (Regisil). The decrease in the peak area of the gc trace at the retention time of each alcohol resulting from silylation was taken as an indication of the amount of alcohol originally present. The alcohol content measured in this way varied from 0 to 2% of the product mixture, depending upon the run. The alcohol is assumed to come from partial hydrolysis of the chloride during work-up[32] and is counted as chloride in Table II.

The area percentages obtained from the gc traces were converted to mole percentages by use of the relative response values for the chlorides, olefin, and olefin addition products. The isomeric acetates were shown to have identical responses, and the isomeric chlorides were assumed to have identical responses. In order to determine the response factor of the olefin addition products, a weighed amount of olefin containing a weighed amount of acetate was treated with chlorine in acetic acid. Since the relative molar amounts of olefin and acetate were now known, the relative gc responses could be calculated directly from the peak areas of the gc trace. In this way, the difficult process of identifying the olefin addition products was circumvented. The product distributions are summarized in Table II.

Preparation[33] and Thermolysis[23] of Chlorocarbonates (I-OCOCl).—Each alcohol, Ia-OH and Ie-OH, was esterified at −78° (Dry Ice–acetone bath) in ether solution with phosgene.[33] Addition of the alcohol solution to the phosgene solution was interrupted several times to permit resaturation of the ether solution with phosgene. The solution was stirred at −78° for 3 hr and then overnight at room temperature under a slow nitrogen flow to ensure removal of all excess phosgene and ether from the mixture, leaving crystalline product in the flask. The Ie-OCOCl product was substantially pure, nmr (CCl_4) δ 4.70 (CHOCOCl), no absorptions for Ie-OH. The Ia-OCOCl product was contaminated with unreacted Ia-OH, nmr (CCl_4) δ 5.12 (CHOCOCl) and 4.04 (CHOH), relative intensities 2:1. Both of these products were used without further purification.

Each chlorocarbonate was decomposed by refluxing a *p*-dioxane solution of it for 1.5–2 hr.[23] The mixture was then analyzed by gc (12 ft XF-1150 column at 120°). From the Ie-OCOCl mixture, the peaks for Ia-Cl and Ie-Cl were in the ratio 21:79 (a:e) and accounted for 55% of the gc trace area. Five peaks of longer retention time were not identified. From the Ia-OCOCl mixture, the peaks for Ia-Cl and Ie-Cl were in the ratio 63:37 (a:e) and accounted for 48% of the gc trace area. The alcohol Ia-OH, which contaminated the starting chlorocarbonate (33%), accounted for 27% of the gc trace area, and an unidentified peak accounted for the remaining 25%.

Preparation of 1-Methyl-4-*tert*-butylcyclohexanols.—A 1:1 mixture of IIIa-OH and IIIe-OH was obtained from the reaction of 4-*tert*-butylcyclohexanone and methylmagnesium iodide in ethyl ether solution. Separation of the isomeric alcohols on alumina[34] proved to be extremely tedious, and not well suited to obtaining large amounts of isomerically pure material. Therefore, the alcohols were esterified by refluxing with acetic anhydride and sodium acetate, and the mixture of acetates was distilled through a spinning band column. The distillation was discontinued when a solid blocked the condenser. Gc analysis showed the liquid [nmr (CCl_4) δ 0.84 (s, *tert*-butyl), 1.42 (s, 1-CH_3), and 1.92 (s, $OCOCH_3$)] and the solid [mp 47–49°; nmr (CCl_4) δ 0.85 (s, *tert*-butyl), 1.47 (s, 1-CH_3), and 1.88 (s, $OCOCH_3$)] to be the separated components of the acetate mixture. Hydrolysis of the liquid acetate[35] (IIIa-OAc) gave IIIa-OH: mp 70–71° (lit.[34,35] mp 70.5–71°); nmr ($DCCl_3$) δ 0.87 (s, *tert*-butyl), 1.20 (s, 1-CH_3). Hydrolysis of the solid acetate[35] (IIIe-OAc) gave IIIe-OH: mp 96–97.5° (lit.[34,35] mp 97.5–98°); nmr ($DCCl_3$) δ 0.87 (s, *tert*-butyl), 1.22 (s, 1-CH_3).

Chlorodehydroxylation[36] of 1-Methyl-4-*tert*-butylcyclohexanols.—Hydrogen chloride gas was passed over 1.0 g of IIIe-OH until all of the alcohol had liquefied. The water layer was removed with a pipet, excess hydrogen chloride was removed at reduced pressure, and the mixture was flushed with nitrogen. Gc analysis (12 ft XF-1150 column at 110°) of the residue showed peaks at 3.4 and 4.7 min in a ratio of 82:18. No alcohol was present. Similar treatment of IIIa-OH gave the 3.4- and 4.7-min peaks in a ratio of 78:22, and a mixture of the alcohols gave the peaks in a ratio of 82:18.

Anal. Calcd for $C_{11}H_{21}Cl$: C, 70.0; H, 11.2. Found: C, 70.4; H, 11.6.

The two chlorides were separated on a Perkin-Elmer F21 preparative gas chromatograph equipped with a 10 ft × 0.25 in. 5% Carbowax 20M column at 80°. The 100-MHz nmr spectra of the separated chlorides ($\geq$90% isomerically pure) were examined in order to determine the line width of the absorption of the 1-methyl group, and from that the configuration of the isomer.[27] For each stereoisomer, four scans were made with at least three different rf field values[37] at a sweep width of 50 Hz. The samples were dissolved in $CDCl_3$, benzene was used for the external lock, and tetramethylsilane was added as an internal standard. The difference in line width at half height of the signals for the 1-methyl group and tetramethylsilane, ΔW_H, was calculated. The chloride comprising about 80% of the product mixture was found to have an average ΔW_H value of 0.19 $\pm$ 0.03 cps, which indicates an equatorial methyl group.[27] The chloride present as about 20% of the product mixture had an average ΔW_H value of 0.66 $\pm$ 0.10 cps, which indicates an axial methyl group[27] having long-range coupling with the axial protons of the adjacent methylene groups. The lower precision in the case of the axial methyl resulted from the shape of the methyl absorption, which made the choice of the base line less obvious than in the case of the equatorial methyl.

Hydrogen Chloride Addition to IV.—Olefin IV was prepared by the dehydration of III with phosphorus oxychloride in pyridine solution[38] and was purified by distillation through a spinning band column: bp 75° (11 mm); nmr (CCl_4) δ 0.86 (s, *tert*-butyl), 1.6 (n m, $CH_3C{=}C$), 5.33 (m, $HC{=}C$). Hydrogen chloride gas was bubbled into a solution of IV (0.5 ml) in methylene chloride (1.0 ml) during 40 min, and the system was then flushed with nitrogen to remove excess hydrogen chloride. Gc analysis (6 ft

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[32] Kwart and coworkers[16a] traced the 2-phenyl-2-butanol in the product mixture from the chlorinolysis of 2-phenyl-1-methylpropyl 2,4-dinitrobenzenesulfenate to the hydrolysis of the corresponding chloride.

[33] K. L. Oliver and W. G. Young, *J. Amer. Chem. Soc.*, **81**, 5811 (1959).

[34] W. J. Houlihan, *J. Org. Chem.*, **27**, 3860 (1962).

[35] C. H. DePuy and R. W. King, *J. Amer. Chem. Soc.*, **83**, 2743 (1961).

[36] (a) H. C. Brown, R. S. Fletcher, and R. B. Johannesan, *ibid.*, **73**, 212 (1951); (b) H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

[37] L. M. Jackson and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," 2nd ed, Pergamon Press, New York, N. Y., 1969, p 314.

[38] B. Cross and G. H. Whitham, *J. Chem. Soc.*, 3892 (1960).

Carbowax 20M column at 110°) of the product mixture showed 65% IIIa-Cl and 35% IIIe-Cl. In a second experiment, the relative amounts of the two chlorides were 64% IIIa-Cl and 36% IIIe-Cl.

Hydrogen Chloride Addition to V.—Olefin V was prepared by the reaction of 4-*tert*-butylcyclohexanone with methylene iodide and magnesium turnings in ethyl ether solution.[39] Distillation of the product mixture through a spinning-band column gave >99% pure V,[39] bp 78° (18 mm), nmr (CCl_4) δ 4.52 (m, 2, $C{=}CH_2$). Hydrochlorination and product analysis were carried out in the same manner as for addition to IV. In two experiments, the IIIa-Cl:IIIe-Cl isomer ratios were 70:30 and 69:31.

Registry No.—*cis*-I (X = CO_2H), 943-28-2; *trans*-I (X = CO_2H), 943-29-3; *cis*-I (X = OSDNP), 37816-62-9; *trans*-I (X = OSDNP), 37816-63-0; *cis*-I (X = OCOCl), 15595-62-7; *trans*-I (X = OCOCl), 15595-61-6; *cis*-I (X = OH), 937-05-3; *trans*-I (X = OH), 937-06-4; *cis*-I (X = OAc), 10411-92-4; *trans*-I (X = OAc), 1900-69-2; *cis*-I (X = Cl), 13131-74-3; *trans*-I (X = Cl), 13145-48-7; *cis*-II (X = OAc), 20298-72-0; *trans*-II (X = OAc), 20298-71-9; *cis*-III (X = OAc), 15807-53-1; *trans*-III (X = OAc), 15807-52-0; *cis*-III (X = OH), 16980-55-5; *trans*-III (X = OH), 16980-56-6; *cis*-III (X = Cl), 25276-09-9; *trans*-III (X = Cl), 25276-10-2; IV, 3419-74-7; V, 13294-73-0; 4-*tert*-butylbenzoic acid, 98-73-7; 4-*tert*-butyl-1-cyclohexene, 2228-98-0; 2,4-dinitrobenzenesulfenyl chloride, 528-76-7; 4-*tert*-butylcyclohexanone, 98-53-3.

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[39] G. Cainelli, F. Bertini, P. Gasselli, and G. Zubioni, *Tetrahedron Lett.*, 5153 (1967).

α-Fluoro-3,3,5,5-Tetrasubstituted Cyclohexanones. I. Synthesis and Conformational Analysis[1]

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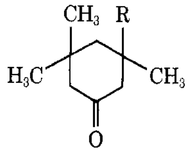
A series of new α-fluoro- and α,α-difluoro-3,3,5,5-tetrasubstituted cyclohexanones has been synthesized by the reaction of perchloryl fluoride with the α-hydroxymethylene derivatives of the following tetrasubstituted cyclohexanones: 3,3,5,5-tetramethylcyclohexanone (**1a**), 3-phenyl-3,5,5-trimethylcyclohexanone (**1b**), and 3-(1-naphthyl)-3,5,5-trimethylcyclohexanone (**1c**). The monofluoro derivative of **1a**, the six possible mono- and difluoro derivatives of **1b**, and the three fluoroketones formed by substitution at C-6 of **1c** have been prepared and characterized. The axial or equatorial nature of the fluorine substituent has been studied as a function of solvent polarity by dipole moment measurements, infrared spectroscopy, and proton and fluorine nmr spectra. All of the results are consistent with the generalization that the fluorine of α-halocyclohexanones has a much greater preference to be equatorial in polar solvents than in nonpolar solvents. Anomalously high-field methyl resonances in the proton nmr spectra of the aryl-substituted fluoroketones furnish a sensitive indicator of the conformational equilibrium, and these lead to the conclusion that a 1,3-diaxial methyl–phenyl interaction is favored over a 1,3-diaxial dimethyl interaction by approximately 0.9 kcal/mol. The chemical shifts of the ring protons are consistent with chair conformations.

Recent work in this laboratory has been concerned with the nmr spectra and conformational analysis of highly substituted cyclohexanones and their derivatives. In these investigations[4-6] particular attention has been given to 3,3,5,5-tetrasubstituted cyclohexanones (*e.g.*, **1**), since, if these molecules are to exist in chair (or at least chairlike) conformations, a severe steric interaction between the axial substituents at C-3 and C-5 is inevitable.



1a, R = methyl
b, R = phenyl
c, R = 1-naphthyl

The proton nmr spectrum of 3,3,5,5-tetramethylcyclohexanone (**1a**) consists of three peaks which correspond to the methyl protons, the γ-methylene protons, and the α-methylene protons. This chemical equivalence is certainly due to a rapid interconversion between conformers. Although the magnitude of a 1,3-diaxial dimethyl interaction has been shown[7] to be approximately 3.7 kcal/mol, a calculation[8] of the conformational enthalpies of **1a** by the Westheimer method indicates that the chair conformer is favored over the most stable boat form by 3.8 kcal/mol. The 2-bromo and 2,6-dibromo derivatives of **1a** have been extensively studied.[9-14] Owing to the 1,3-diaxial interaction in these compounds, Ourisson, *et al.*,[9,10] have postulated the "reflex effect" by which the cis axial methyl groups are bent outward, causing the α carbons to be pushed together. In a study[11] of the crystal structures of 2-bromo- and *cis*-2,6-dibromo-3,3,5,5-tetramethylcyclo-

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[1] Taken in part from the Ph.D. dissertation submitted by M. M. Chrysam III to the Department of Chemistry, Texas A & M University, 1970; this work was initiated at the Chemistry Department of the Illinois Institute of Technology, Chicago, Ill.

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