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THE STEREOCHEMISTRY OF PRODUCT FORMATION FROM SOME 4-*t*-BUTYLCYCLOHEXYL CATIONIC INTERMEDIATES[1]

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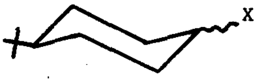
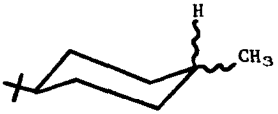
Although the literature contains many reports of investigations into the stereochemistry of both carbonium ions and cyclohexyl rings, there is a surprising paucity of data providing useful information about the stereochemistry of product formation from cyclohexyl cations. A number of reactions involving cyclohexyl cations have been reported,[3] but in all of these reactions the stereochemistry of the major products is directly tied to the stereochemistry of the reactant. In the present study, the preferred stereochemical paths of product formation from a number of different cyclohexyl carbonium ion precursors have been determined and compared.

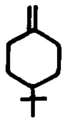


I-X



II-X

III



IV

cis- and *trans*-4-*t*-Butylcyclohexanecarboxylic acids (Ia-COOH and Ie-COOH, respectively)[4] were separately decarboxylated by two cationic processes and, for comparison, by one radical process. Anodic oxidation in aqueous solution[5] of each acid gave a product mixture consisting of olefin and *cis*- and *trans*-alcohols (Ia-OH and Ie-OH). While Ie-OH was the major alcohol product from both acids, its predominance in the mixture from Ie-COOH was substantially greater than it was from Ia-COOH. (See Table 1 for summary of data.) The carbonium ion intermediate in this electrolysis thus does not appear to be free from the influence of the stereochemistry of the starting acid.

Table 1. Summary of Reactions with 4-*t*-Butylcyclohexyl Systems.

Reactant[a]	Reaction	Products (R-X)	% Axial R-X
Ia-COOH	Anodic Oxid.	I-OH	46
Ie-COOH	Anodic Oxid.	I-OH	30
Ia-COOH Ie-COOH	$Pb(OAc)_4$, HOAc[b]	I-OAc	53
Ia-COOH Ie-COOH	$Pb(OAc)_4$, LiCl[c]	I-Cl	67
Ia-OCOCl	Thermolysis	I-Cl	63
Ie-OCOCl	Thermolysis	I-Cl	21
IIa-OH IIe-OH	HCl	II-Cl	80
III	HCl	II-Cl	65
IV	HCl	II-Cl	70

a) Ref. 4. b) Product formation from cationic intermediate.[5]
c) Product formation from radical intermediate.[7]

By lead tetraacetate oxidative decarboxylation, the acids were converted to olefin and alkyl acetates (Ia-OAc and Ie-OAc) through alkyl cation intermediates.[6] From the isomeric acids, mixtures containing the same proportions of Ia-OAc and Ie-OAc were obtained, and, in contrast to the anodic oxidations, axial product is slightly favored over equatorial product. Halodecarboxylations of the two acids by lead tetraacetate in the presence of lithium chloride, a radical process,[7] also gave product mixtures (alkyl chlorides) indistinguishable from each other, with axial product predominating 2:1. 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 by oxidation.

Thermal decomposition of chlorocarbonates has recently been described by an ion pair mechanism.[8] Thermal decomposition of *cis*- and *trans*-4-*t*-butylcyclohexyl chlorocarbonates, obtained from the reaction of phosgene with the isomeric 4-*t*-butylcyclohexanols, yielded the configurationally retained chloride as the major chloride product, suggesting the intervention of an S_Ni mechanism with little competition from a "free" carbonium ion intermediate.

Some reactions of related tertiary carbonium ions have been compared with the above reactions of secondary carbonium ions. Addition of hydrogen chloride gas to isomerically pure 1-methyl-*cis*- or -trans-4-*t*-butylcyclohexanol (IIa-OH and IIe-OH) and to each of the isomeric olefins, 1-methyl-4-*t*-butyl-1-cyclohexene (III) and 1-methylene-4-*t*-butylcyclohexane (IV), yields chloride products arising from a tertiary cyclohexyl cation intermediate. The isomeric alcohols gave identical product mixtures rich in axial chloride.[9,11] Both olefins also gave mainly axial chloride. The preference for axial attack may stem from torsional interactions, as has been proposed for cyclohexyl radicals.[12] Attack on the essentially planar cyclohexyl cation 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 II-Cl to 53:47 for I-OAc).

Therefore, 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.

REFERENCES

1. Based on the Ph.D. dissertation of S.D.E., Louisiana State University - Baton Rouge, Jan., 1971. Grateful acknowledgement 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.

2. National Aeronautics and Space Administration Trainee, 1966-69.

3. For examples, see S. Winstein and N.J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955), and W. Hückel and K. Heyder, *Chem. Ber.*, **96**, 220 (1963).

4. 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.

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8. J.L. Kice and G.C. Hanson, *Tetrahedron Letters*, 2927 (1970).

9. The stereoisomeric chlorides were differentiated by comparing the line widths at half height of the $ClCCH_3$ absorptions in the nmr spectra of the two compounds; the axial-CH_3 absorption is broader than the equatorial one.[10]

10. C.W. Shoppee, F.P. Johnson, R.E. Lack, J.S. Shannon, and S. Sternhell, Tetrahedron Suppl., No. 8, Part II, 421 (1966).

11. Before the advent of common use of gas chromatography and nuclear magnetic resonance techniques for mixture analysis, H.C. Brown, R.S. Fletcher, and R.B. Johannesen [J. Amer. Chem. Soc., **73**, 212 (1951)] reported that the stereoisomeric 1,3-dimethyl-1-cyclohexanols reacted with HCl to form tertiary chloride products, which were not distinguishable by hydrolysis kinetic data. These data indicated that the chloride was either a single compound or a mixture of compounds which reacted at the same rate. When our mixture of 4-*t*-butyl-1-methylcyclohexyl chlorides was treated with a deficiency of base, the isomeric composition of the chloride mixture was unchanged by olefin formation.

12. F.R. Jensen, L.H. Gale, and J.E. Rodgers, J. Amer. Chem. Soc., **90**, 5793 (1968).