the bulky chlorine atoms would be expected to decrease the reactivity, due to steric hindrance. On the other hand, the inductive effect of chlorine atoms on the π-bond electron would tend to facilitate the addition of nucleophilic alkyl radicals. The overall effect of chlorine substitution is reflected in the reactivity order: C_2Cl_3H > *trans*-$C_2Cl_2H_2$ > *cis*-$C_2Cl_2H_2$ > C_2Cl_4. The data in Table VII would seem to indicate that the steric and inductive effects influence both the activation energy and the preexponential factor.

Mechanistic Partition of the Solvolysis of Cyclohexyl Tosylate

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Abstract: The substitution and elimination products from the solvolysis of cyclohexyl tosylate have been quantitatively apportioned into direct and rearranged components by examination of the reactions of cyclohexyl-*1-d* and cyclohexyl-*2,2,6-d*$_3$ (1 H trans to 6 H) tosylates. The substitution product (cyclohexyl ester) comes from two sources: (1) direct substitution at the 1 position exclusively with inversion, and (2) rearrangement *via* a hydride shift with subsequent substitution at a carbon adjacent to the original 1 position. The elimination product (cyclohexene) likewise is composed of material formed before and after hydride shift. The direct substitution product decreases from 80% in buffered acetic acid to 60% in formic acid, and to about 50% in trifluoroacetic acid, with the remainder composed entirely of hydride-shifted material. No direct substitution with retention was detected, although the question could not be fully resolved for trifluoroacetolysis. The elimination product is formed in acetic acid with <5% hydride shift, in formic acid with 15% shift, and in trifluoroacetic acid with 50% shift. Rearrangement in the elimination process thus lags behind that in the substitution process except in trifluoroacetic acid. The results are discussed in terms of rate-determining formation of an intimate ion pair, followed by partitioning into the various reaction pathways. When the amounts of all the various product components from acetolysis were assessed, the product distribution proved to be essentially identical with that from *trans*-4-*tert*-butylcyclohexyl tosylate.

Considerable effort has been devoted to the study of the solvolysis mechanism of substituted cyclohexyl arenesulfonates.[2] The process of solvolysis results in products formed by substitution (cyclohexyl esters) and by elimination (cyclohexene). A significant portion of these products arises from substitution or elimination that follows a 2,1-hydride shift. In order to detect this type of rearrangement in the cyclohexyl series, a positional label must be installed in the ring. Thus an alkyl group in the 4 position would be found in the 3 position of rearranged material obtained from substitution. Separation and analysis of the positional isomers permit a direct determination of the amount of rearrangement. In order to determine the stereochemistry of the substitution component of the reaction, the system is in further need of a diastereomeric label, *e.g.*, an alkyl group at the 4 position with known stereochemistry with respect to the arenesulfonate leaving group. Thus a complete analysis of the reaction components requires determination of the overall ratio of substituton to elimination, of the proportion of rearranged to unrearranged products, and of the stereochemistry of the substitution component.

A diastereomeric label that permits a complete analysis of all the reaction components is the 4-*tert*-butyl group. The solvolysis of *cis*- and *trans*-4-*tert*-butylcyclohexyl arenesulfonates was first studied by Winstein and Holness[2a] and more recently with more reliable analytical accuracy by Whiting and coworkers.[2d] The trans isomer, for example, on acetolysis gives 0.4% of the *trans*-4-alkyl ester (substitution, unrearranged, retention), 19.5% of the *cis*-4-alkyl ester (substitution, unrearranged, inversion), 2.0% of the 3-alkyl esters (substitution, rearranged), 73.6% of the 4-alkylcyclohexene (elimination, unrearranged), and 5.6% of 1- and 3-alkylcyclohexenes (elimination, rearranged). The ene/ester ratio therefore is 79.2:21.9, the unrearranged/rearranged ratio is 93.5:7.6, and the inversion/retention ratio (1 position) is 19.5:0.4.

Although the diastereomeric label is an effective device to dissect the reaction pathways of substituted cyclohexyl arenesulfonates, the question naturally arises as to the nature of the solvolysis of the totally unsubstituted (except at the 1 position) cyclohexyl arenesulfonate. The alkyl-substituted derivatives may be poor models for the unsubstituted material for several reasons. The bulky *tert*-butyl group, although having the advantage of freezing the ground state into a known conformation, by the same token imparts some ground-state distortion. X-Ray structures are

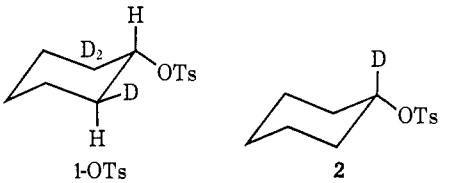
(1) (a) This work was supported by the Petroleum Research Fund, administered by the American Chemical Society (Grant 2970-AC4), and by the National Science Foundation (Grant GP-35868X); (b) NDEA Fellow, 1968–1971; NASA Trainee, 1971–1972. For an earlier report on some of this work, see J. B. Lambert, G. J. Putz, and C. E. Mixan, *J. Amer. Chem. Soc.*, **94**, 5132 (1972).

(2) For leading references, see (a) S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955); (b) V. J. Shiner, Jr., and J. G. Jewett, *ibid.*, **87**, 1382, 1383 (1965); (c) J. L. Mateos, C. Perez, and H. Kwart, *Chem. Commun.*, 125 (1967); (d) 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); (e) M. Tichy, J. Hapala, and J. Sicher, *Tetrahedron Lett.*, 3739 (1969); (f) J. E. Nordlander and T. J. McCrary, Jr., *J. Amer. Chem. Soc.*, **94**, 5133 (1972).

now available for *cis*- and *trans*-4-*tert*-butylcyclohexyl tosylate,[3] and small distortions in the ring are present. The cis compound, for example, with an axial tosylate group is flattened in order to relieve axial–axial interactions. It is doubtful that these ground-state distortions appreciably alter the mechanism of solvolysis. The presence of the *tert*-butyl group, however, can have a critical effect on the nature of the solvolysis transition state. The steric interactions of the group are sufficiently large to exclude certain transition-state geometries, such as those that require the group to be axial. For example, if the departure of the tosylate group occurred preferentially from the axial position, the *cis*-4-*tert*-butyl compound would be well positioned in the ground-state conformation. The trans isomer, however, would either have to convert to a nonchair form in order to avoid an axial *tert*-butyl group or undergo reaction by equatorial departure of tosylate. In this manner, the alkyl label could exclude the very transition state by which the unsubstituted material solvolyzes. Thus the label is necessary to determine the product distribution, but its very presence can destroy the relevance of the result to the unsubstituted system.

Several partially successful methods have been devised to circumvent this "uncertainty principle" problem. Physical constants (kinetic isotope effect,[4] overall rate[2c]) can be measured for the unsubstituted system and compared with those for the alkyl-labeled material. Although this procedure can lead to useful mechanistic conclusions, it gives no information regarding the make-up of the product distribution in the unsubstituted system. Nordlander and McCrary[2f] used the subtle label of CH_3CCD_3 group at the 4 position, together with arguments that a *gem*-dimethyl group, unlike a *tert*-butyl group, does not alter the transition-state geometry, in order to obtain the unrearranged/rearranged and inversion/retention ratios. Operating on the totally unsubstituted system, Reutov and coworkers[5] utilized a ^{14}C label to measure the unrearranged/rearranged ratio in the ester, although no stereochemical information could be obtained.

In order to formulate a complete description of the products from the solvolysis of unsubstituted cyclohexyl tosylate, we have prepared and studied a pair of deuterium-labeled substrates. For a stereochemical label, we use a single proton, rather than an alkyl group. Compound **1** was prepared as described in the next section. There is only one proton vicinal to the leaving group, since the remaining three vicinal protons have been replaced by deuterium. The known stereochemical relationship between the 1 and 6 protons is reflected in the vicinal coupling constant. The coupling constant in the solvolysis product ester indicates whether the reaction has taken place by retention or inversion. The use of a diastereomeric proton label obviates the problems associated with the *tert*-butyl groups. It is doubtful that the difference in size between hydrogen and deuterium will have a palpable effect on the stereochemical outcome of the solvolysis.



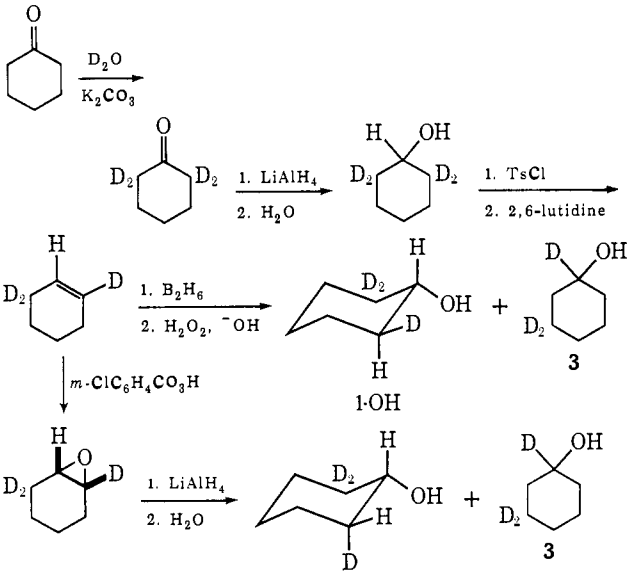
Although compound **1** is useful for determining the stereochemistry of the reaction, it cannot serve as a means to measure the extent of hydride-shift rearrangement. For this purpose, we prepared cyclohexyl-*1-d* tosylate (**2**). Location of the deuterium label by integration of appropriate peaks in the nmr spectrum permits determination of the extent of rearrangement in both the ester and the alkene products.

The above experiments were carried out in acetic, formic, and trifluoroacetic acids, buffered with their conjugate bases. The combination of labeling experiments showed that, to the limit of the accuracy of the method (>95%), the unrearranged ester is formed with inversion of configuration in acetic and formic acids. The extent of hydride shift increases from acetic to formic to trifluoroacetic acid. For acetic and formic acids, the ester component contains a larger proportion of rearranged material than the alkene component.

Results

Cyclohexyl tosylate fully deuterated at the 1 position (**2**) was obtained by reduction of cyclohexanone with lithium aluminum deuteride, followed by treatment of the alcohol with tosyl chloride according to standard procedures.[6] Preparation of cyclohexyl-*2,2,-6-d*$_3$, in which the 1 and 6 protons are trans to each other, was accomplished by a method similar to one described by Shiner and Jewitt[2b] (Scheme I). Exchange of the α protons of cyclohexanone for deuterium, followed by hydride reduction gave the labeled (d_4) alcohol. Conversion of the alcohol to the tosyl-

Scheme I



(3) P. L. Johnson, C. J. Cheer, J. P. Schaefer, V. J. James, and F. H. Moore, *Tetrahedron*, **28**, 2893 (1972); P. L. Johnson, J. P. Schaefer, V. J. James, and J. F. McConnell, *ibid.*, **28**, 2901 (1972).

(4) W. H. Saunders, Jr., and K. T. Finley, *J. Amer. Chem. Soc.*, **87**, 1384 (1965).

(5) T. N. Shatkina, E. V. Leont'eva, and A. O. Reutov, *Dokl. Akad. Nauk SSSR*, 177, 373 (1967). This paper is incorrectly abstracted in *Chem. Abstr.*, **68**, 86861v (1968).

(6) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

ate and elimination with the aid of 2,6-lutidine as base gave cyclohexene-*1,3,3-d*$_3$. Hydroboration and oxidation of this alkene gave an approximately 50:50 mixture of the stereospecifically labeled alcohol **1** and an undesired alcohol **3**. Because the stereospecificity of the solvolysis reaction is to be assessed by examining the splitting pattern of the 1-proton resonance (*vide infra*), the presence of **3** in the reaction mixture is totally irrelevant. The labeling pattern of **1**, however, is unsuitable for assessing the amount of hydride shift. Furthermore, if there is a large proportion of hydride shift, the label is stereochemically less operational. For this reason, the amount of hydride shift was independently assessed for each solvent by means of compound **2**.

To confirm the stereochemistry of the tosylate obtained after the hydroboration sequence of Scheme I, the coupling constant between the 1 and the 6 protons was measured. Spectra were taken at −80° to slow down the process of ring reversal, and the deuterium resonance frequency was irradiated to remove proton–deuterium couplings. These conditions were used for all measurements of this coupling constant, but will henceforth not be specified. The resonance of the axial 1 proton in the equatorial isomer of the starting tosylate is a doublet, centered at δ 4.2 with a splitting of 10.1 Hz. This coupling constant, typical for the axial–axial relationship, confirms the trans stereochemistry between the 1 and 6 protons.

For the sake of comparison, cyclohexyl-*2,2,6-d*$_3$ acetate was prepared in both stereomodifications (1 proton cis and trans to the 6 proton) from the alcohols shown in Scheme I. The doublet for the trans material was centered at δ 4.4 with a splitting of 10.3 Hz (Figure 1). The doublet for the cis material was also centered at δ 4.4, and exhibited a splitting of 3.8 Hz. The cis alcohol was obtained from cyclohexene-*1,3,3-d*$_3$ by epoxidation and hydride reduction (Scheme I).

Acetolysis of cyclohexyl-*2,2,6-d*$_3$ (1 H trans to 6 H) tosylate was accomplished by heating the substrate in acetic acid containing 1.1 equiv of potassium acetate and 4% by volume acetic anhydride at 95° for 20 hr (about 45 half-lives[7]). Vapor phase chromatography of the product mixture showed 81% cyclohexene and 19% cyclohexyl acetate. Stability tests demonstrated that both products remained unchanged under the reaction conditions.

The spectrum of the product acetate (axial 1 proton) is given in Figure 1. The resonance is composed of a doublet, centered at δ 4.4 with a splitting of 3.8 Hz. The spectrum is essentially identical with that of the acetate obtained directly from the alcohol with the 1 and 6 protons cis to each other. During the course of the reaction, the trans relationship between the protons was therefore converted to a cis relationship. Computer simulation of this spectrum indicated that it consists of 80–85% of a doublet with 3.8 Hz splitting. The remaining 15–20%, as will be seen, arises from a hydride-shift process rather than from a retention mechanism, and causes a small broadening at the base of the doublet (Figure 1).

Acetolysis of cyclohexyl-*1-d* under the same conditions yielded cyclohexyl acetate in which 21% of a

(7) J. B. Lambert, H. G. Smith, Jr., and A. P. Jovanovich, *J. Org. Chem.*, 35, 3619 (1970).

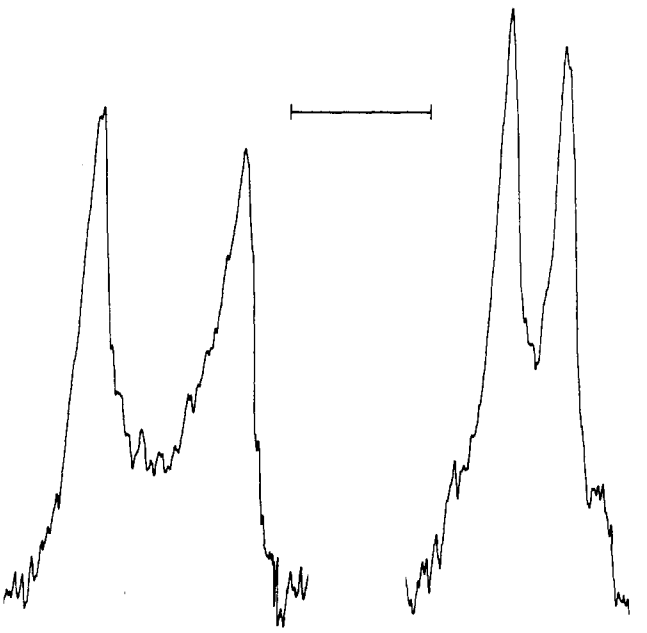


Figure 1. (Left) The axial 1-proton resonance of cyclohexyl-*2,2,6-d*$_3$ (1 H trans to 6 H) acetate. The spectrum is taken at 90 MHz, −80°, with deuterium decoupling, in CS_2–$CHCl_3$ (5:4) with 10% TMS by volume, and averaged over four transits. The spectrum of the corresponding tosylate is essentially identical. The calibration bar represents 10 Hz. (Right) The axial 1-proton resonance of cyclohexyl acetate produced in the acetolysis of cyclohexyl-*2,2,6-d*$_3$ (1 H trans to 6 H) tosylate. The spectrum is taken at 90 MHz, −80°, with deuterium decoupling, in CS_2 with 10% by volume TMS, and averaged over four transits.

unit proton resonance was present for the 1 proton, as determined by comparison with the integral of the methyl resonance. This figure represents the amount of hydride shift. In the spectrum of the cyclohexene product, the ratio of alkenic protons to all other protons was 0.130. This ratio (Table I) indicates that

Table I. Intensity Ratio between Alkenic Resonances and All Others in Cyclohexene as a Function of Hydride-Shift Proportion[a,b]

Hydride shift, %	Ratio[c,d]	Ratio[d,e]
0	0.125	0.125
5	0.131	0.130
10	0.136	0.136
20	0.147	0.146
40	0.170	0.168
50	0.181	0.179
60	0.192	0.189
80	0.215	0.211
100	0.237	0.232

[a] Assuming only a single hydride shift. [b] These calculations take into account the fact that the product of elimination without rearrangement is also one of the products of elimination following rearrangement. [c] Assuming no primary deuterium isotope effect. [d] The ratio was calculated by inspection for the cases of 0 and 100% hydride shift, and was interpolated for the remaining cases. [e] Assuming an infinite primary deuterium isotope effect.

only about 5% hydride shift occurs before the cyclohexene is formed.

Formolysis of **1** was carried out at 25° for 30 hr in formic acid containing 1.1 equiv of sodium formate. Under these conditions, both the ester and the alkene

products were stable. Under harsher conditions (50°, 22 hr), however, the alkene product slowly added the elements of formic acid. The spectrum of the substitution product (cyclohexyl formate) contained an axial 1-proton resonance composed of a doublet centered at δ 4.6 with a splitting of 4.0 Hz. Computer simulation indicated that the 4.0-Hz doublet comprised 55–60% of the resonance, with the remainder present as a broadening at the base. Again, the primary pathway is substitution with inversion, and the remainder can be entirely accounted for by the hydride-shift process.

Formolysis of the tosylate **2** produced cyclohexyl formate in which 44% of the 1 position contained a proton rather than a deuteron, as determined by comparison of the 1-proton and the formyl integrals. The ratio of alkenic resonances to those from all other protons in the cyclohexene product was 0.139, corresponding to 10–15% hydride shift preceding elimination (Table I).

Because formic anhydride is not a practicable substance for keeping formic acid dry, a small amount of water was present in the solvent. As a result, some cyclohexanol was formed during the solvolysis. From unlabeled cyclohexyl tosylate, 79% of the alkene, 8% of the formate, and 13% of the alcohol were formed. From **1**, the respective percentages are 81, 14, and 5%; from **2**, they are 78, 15, and 7%. Small changes in the proportion of cyclohexanol cannot be considered significant since the amount of water present was variable. The alcohol could be formed either by direct displacement on tosylate, or by addition to first-formed cyclohexene. Integration of the axial 1-proton resonance of the alcohol produced from **2** showed that 24% of a unit proton resonance was present.

The solvolysis of cyclohexyl tosylate in trifluoroacetic acid containing 1.1 equiv of sodium trifluoroacetate and 10% by volume trifluoroacetic anhydride was found to have a half-life of only about 35 min at 25°, measured by monitoring peak heights of the tolyl methyl resonances. Addition of trifluoroacetic acid to cyclohexene formed in the reaction takes place with a half-life of about 30 min at 37°, even under the buffered conditions. This elimination–addition process destroys the labels in both **1** and **2**. Isolation of products was therefore made after only 50 min at 25° (about 1.5 solvolysis half-lives) in order to maintain the integrity of the label. Under these conditions, the reaction mixture consisted of about 70% cyclohexene and 30% ester, although the percentages are somewhat compromised by the concurrent addition reaction.

The ester product from trifluoroacetolysis of **1** contained an axial 1-proton resonance with a flat top and a width at half height of 17 Hz. Because scrambling due to elimination–addition had been avoided, scrambling from the hydride-shift process must have been considerable. No firm conclusions about the stereochemistry of the substitution at the 1 position could be made, although it was clear that substitution without rearrangement was in a smaller proportion than in acetic or formic acids.

Although the cyclohexene product adds trifluoroacetic acid under the reaction conditions, cyclohexyl trifluoroacetate itself is stable. Cyclohexyl-*1-d* trifluoroacetate subjected to the conditions of the reaction lost no deuterium from the 1 position.

Solvolysis of **2** for 1.5 half-lives produced a trifluoroacetate in which hydride shift had occurred to the extent of 50%. The ratio of alkenic resonances to others in the alkene product (0.175) represented 45–55% of hydride shift prior to elimination (Table I).

To explore the extent of solvent addition in the reaction, several solvolyses were carried out in CF_3CO_2D, and deuterium incorporation was monitored by mass spectrometry. The ratio of peaks 197/196 for unlabeled cyclohexyl trifluoroacetate is 0.15; for cyclohexyl-*1-d* trifluoroacetate it is 4.1. The ratio found for the ester produced by solvolysis of unlabeled cyclohexyl tosylate in deuterated trifluoroacetic acid was 0.4. As expected, some of the product is formed by elimination–addition, but the amount is too small (~10%) to affect our conclusions. The ratio of peaks 83/82 for unlabeled cyclohexene is 0.066; for cyclohexene-*1-d* it is 3.53. The ratio for the material produced from unlabeled cyclohexyl tosylate in deuterated trifluoroacetic acid is 0.12. Again, there is only a small amount of deuterium incorporation from solvent.

Discussion

Substitution. Of the substitution products in the acetolysis of cyclohexyl tosylate, 80% arise from displacement of tosylate with inversion of configuration and 20% from hydride shift. Our observations alone do not specify whether the displacement occurs on an electrically neutral molecule of cyclohexyl tosylate or on a tight ion pair. The expectation that a solvent-separated ion pair should give some retained material tends to exclude this species. The results exclude symmetrically solvated carbonium ions and symmetrical hydrogen-bridged ions as intermediates.

Strong evidence has been presented from kinetic α-secondary deuterium isotope effect data[2b,4] that the slow step in acetolysis does not directly involve solvent. The observed k_H/k_D value of 1.22 is clearly out of the range for direct displacement reactions (0.95–1.06). The most economical explanation that encompasses both the isotope effect results and our stereochemical results is that the slow step is formation of a tight ion pair or conversion of a tight ion pair to a solvent-separated ion pair.[8] Evidence for ion-pair formation in the solvolysis of 2-octyl mesylate has also been adduced from the use of competitive nucleophiles.[9] The product-determining step in the acetolysis of cyclohexyl tosylate, from the stereochemical results, must then be attack by solvent at the backside of the ion pair at the 1 position.

Formic acid has about the same nucleophilicity as acetic acid[10] but is considerably more ionizing. The conclusions drawn from the formolysis of **1** and of **2** are essentially the same as for the acetolysis. Substitution with inversion at the 1 position occurs to the extent of about 60%, with the remainder of the substitution product formed after a hydride shift. If the displacement is considered to occur on an intimate ion pair, the higher proportion of hydride shift in

(8) V. J. Shiner, Jr., and R. D. Fisher, *J. Amer. Chem. Soc.*, **93**, 2553 (1971).

(9) R. A. Sneen and J. W. Larsen, *ibid.*, **91**, 362 (1969); R. A. Sneen, *Accounts Chem. Res.*, **6**, 46 (1973).

(10) T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 992 (1972).

formolysis than in acetolysis can be attributed to a greater separation of the leaving tosylate group from the 1 carbon.

If it is assumed that cyclohexanol is formed in formolysis by displacement of tosylate by the water impurity in the solvent, then the results with **2** indicate that 24% of the attachment of hydroxyl occurs after a hydride shift has taken place, as compared to 40% for the attachment of formate. The higher nucleophilicity of water can be invoked to explain this observation. It is possible, however, that the cyclohexanol is formed by the addition of the elements of water to cyclohexene, since it was observed that cyclohexanol, not cyclohexyl formate, can be formed when cyclohexene is subjected to buffered formolysis conditions for 30 hr at 25°. Since we had less interest in this aspect of the problem, we did not pursue it further.

Trifluoroacetic acid is much more ionizing and less nucleophilic than either of the other solvents. Because of the possible addition of solvent to cyclohexene under the conditions of the solvolysis, it was imperative to establish that the ester isolated from the reaction had resulted from a true displacement rather than from an elimination–addition. The rates of the overall solvolysis reaction and of the addition to cyclohexene were measured, and the solvolysis rate happily proved to be the more rapid. Conditions of time and temperature were therefore specified so that little addition could have occurred. The solvolysis was allowed to proceed to about 1.5 half-lives, at which time only a small amount of addition (<10%) was possible. Furthermore, following a reported procedure,[11] we carried out the solvolysis reaction on unlabeled cyclohexyl tosylate in trifluoroacetic acid with deuterium in place of the acid proton. If the ester were formed by addition to cyclohexene, it should contain deuterium. Analysis of the mass spectral data (previous section) showed that at least 80–90% of the trifluoroacetate isolated under our conditions contained no deuterium. The ester examined from our solvolysis reactions therefore is a true product of substitution.

The ester product from the trifluoroacetolysis of **1** gave an axial 1-proton resonance that was not split into a doublet. Apparently so much hydride shift had taken place that the stereochemical label was rendered nonfunctional. The solvolysis of **2** confirmed this result, since it indicated that about 50% of the product came from the hydride-shift process. The more ionizing trifluoroacetic acid therefore brings about an even greater separation between the tosylate ion and the 1-carbon atom in the intimate ion pair or possibly even conversion to a solvent-separated ion pair. As a result, a larger proportion of hydride shift is observed. Whether some displacement with retention at the 1 position begins to appear cannot be answered by the present experiments. The discrepancy between the amount of hydride shift (about 50%) and the very substantial scrambling of the label in **1** (recall, however, the presence of **3**-OTs, which confuses the situation in the presence of hydride shift) admit to the possibility that some retention occurs. This aspect of the reaction could be the subject of further study.

(11) J. J. Dannenberg, D. H. Weinwurzel, K. Dill, and B. J. Goldberg, *Tetrahedron Lett.*, 1241 (1972).

Elimination. Formation of cyclohexene is the dominant reaction pathway (70–80%) in all three solvents. It is interesting that the alkene proportion is so similar in these dissimilar media. Apparently either the factors that control partitioning of the starting material into substitution and elimination modes are independent of solvent ionizing power and nucleophilicity, or multiple effects are canceling.

The proportion of elimination occurring after a hydride shift is solvent dependent. In acetolysis, almost all (95%) of the cyclohexene is formed without prior rearrangement, and in formic acid, 85–90% is so formed. In trifluoroacetic acid, less than 50% of the alkene is formed without rearrangement. These results parallel the observations with substitution, although in acetic and formic acids the proportion of alkene formed after rearrangement is smaller than the corresponding proportion of ester.

One can consider that the first-formed ion-pair intermediate has three options: (1) direct substitution to form the inverted ester; (2) abstraction of the β proton to form cyclohexene without rearrangement; or (3) hydride shift to a new intermediate that has a new set of options available. Rearranged ester and alkene come from this latter intermediate. Evidence described by other workers[2d,f] indicates that ester formation at the new center is also stereoselective, but our experiments do not give information on this point. Because there are different proportions of hydride shift for the substitution and the elimination components in formic and acetic acids, the original intermediate (C-1 functionality) must be somewhat different from the rearranged intermediate (C-2 functionality). We cannot hypothesize as to the differences between these two intermediates with regard to extent of charge formation on carbon, location of solvent, etc., except to note that the second intermediate produces a smaller proportion of elimination. In terms of absolute percentages in acetic acid, for which the best data are available, the overall split between substitution and elimination is 20/80. Of the substitution, about 20% is rearranged; of the elimination, less than 5%. The absolute count therefore is: unrearranged substitution with inversion, 16%; unrearranged substitution with retention, <1%; rearranged substitution, 4%; unrearranged elimination, 76%; rearranged elimination, 4% (or less). It is interesting that the corresponding figures for the acetolysis of *trans*-4-*tert*-butylcyclohexyl tosylate (*vide supra*)[2d] are almost identical: 19, 1, 2, 74, and 6% (approximately 1–2% must also be subtracted from the C-2 functionalized intermediate). This striking similarity of product compositions suggests similar mechanisms and hence an equatorial leaving group for the unsubstituted case. Because of the formation of cyclohexanol in formolysis and the addition to cyclohexene in trifluoroacetolysis, we cannot construct analogous figures for these solvent systems. We can note, however, that in formic acid 40–45% of the substitution product and 10–15% of the elimination product are rearranged, but in trifluoroacetic acid both the substitution and the elimination components are about 50% rearranged. We can conclude therefore that in trifluoroacetic acid there is very little difference between the initial intermediate (C-1 functionality) and the rearranged intermediate (C-2 functionality), since

they partition into almost identical proportions of substitution and elimination.

Conclusions

The α-deuterium isotope effect and the present stereochemical results indicate that the rate-determining step in the acetolysis of cyclohexyl tosylate is formation of a tight ion pair.[12] This intermediate can suffer backside displacement to form inverted cyclohexyl acetate (~16% of the total product) or it can lose a β proton to give cyclohexene (~76%). It can also undergo a hydride shift to form a new intermediate that is functionally active at C-2(C-6). The ratio of ester to alkene (1:1) after rearrangement is proportionately larger than was the case for the C-1 functional intermediate (1:5). Substitution at C-1 occurs entirely with inversion, so that a symmetrically solvated carbonium ion is not present and a solvent-separated ion pair is unlikely. The situation is very similar in formic acid, except that the amount of material rearranged through hydride shift is approximately double that in acetic acid. Again, no substitution product with retained stereochemistry was observed. The higher proportion of rearranged material suggests that the ion pair is further separated in formic acid and that more assistance from neighboring hydrogen is necessary.

The situation is somewhat different in the more highly ionizing trifluoroacetic acid. Our stereochemical label was too thoroughly scrambled by hydride shifts to permit a designation of inversion or retention for the substitution product at C-1. About half of both the substitution and the elimination products were formed after hydride shift. The nearly identical partition between substitution and elimination at both C-1 and C-2 contrasts to the situation in acetic and formic acids. The two intermediates in trifluoroacetic acid must therefore be somewhat similar. Our evidence on trifluoroacetolysis cannot differentiate among or exclude equivalently solvated ion pairs, two symmetrically solvated carbonium ions, or even a symmetrical hydrogen-bridged species, which has recently been suggested in the trifluoroacetolysis of 2-butyl tosylate.[11]

Experimental Section

Melting points were determined in a Hershberg apparatus and are uncorrected. Routine nmr spectra were recorded on a Varian Associates Model T-60 spectrometer. Variable-temperature spectra and deuterium-decoupled spectra were obtained on a 90-MHz Bruker HFX-10 spectrometer, equipped with a Nicolet Model 1074 computer for signal averaging.[13] Analytical vapor phase chromatography was performed on a Varian Aerograph series 1520b instrument with a $^1/_8$ in. × 5 ft column of 5% silicone gum rubber (SE-30) on Chromosorb W. Preparative vapor phase chromatography was performed on an F&M Model 700 instrument with a 0.5 in. × 10 ft column of the same material. Mass spectra were obtained with a CEC Model 21-104 instrument.[13] Computer-simulated nmr spectra were calculated with a CDC Model 6400 computer equipped with a CalComp Model 565 plotter.

Cyclohexyl Tosylates. All tosylates used in this study were prepared by the Tipson procedure.[6]

Cyclohexanol-*2,2,6,6-d*$_4$. Cyclohexanone was treated with successive batches of D_2O (Bio-Rad Laboratories), containing NaCl and K_2CO_3, until the α-proton resonances could no longer be detected by nmr spectroscopy. After the material was dried, filtered, and distilled, it was treated with $LiAlH_4$ in ether. The distilled product was obtained in 74% yield from unlabeled cyclohexanone: bp 70–73° (10–15 mm); nmr (CCl_4) δ 1.8 (broad m, 6, CH_2), 3.9 (m, 1, CH), 4.0 (s, 1, OH). The δ 4.0 peak disappeared when the sample was shaken with a drop of D_2O.

Cyclohexene-*1,3,3-d*$_3$. The alcohol was converted to the tosylate, a solution of which (18 g, 0.07 mol) in 2,6-lutidine (120 ml, freshly distilled from BaO) was heated to reflux (oil bath temperature of 160°). The cyclohexene was allowed to distil out through a 14-cm Vigreux column as it was produced. All material boiling below 95° was collected and used without further purification. Vapor phase chromatography showed the product to be contaminated with about 5% of 2,6-lutidine. The yield of crude material was 5.5 g (90%): nmr (CS_2) δ 1.6 (m, 4, nonallylic CH_2), 2.0 (m, 2, allylic CH_2), 5.6 (m, 1, alkenic).

Cyclohexanol-*2,2,6-d*$_3$ (1 H Trans to 6 H) and Cyclohexanol-*1,3,3-d*$_3$. Diborane was generated by adding 47.5 g (0.33 mol) of boron trifluoride etherate (freshly distilled) to a stirred mixture of 10 g (0.26 mol) of $LiAlH_4$ in 200 ml of anhydrous ether under a nitrogen atmosphere. The nitrogen, containing diborane, was passed through a sintered-glass bubbler into a dry 100-ml tetrahydrofuran solution of 5 g (0.06 mol) of cyclohexene-*1,3,3-d*$_3$. The solution was allowed to sit for 3 hr after addition of the etherate had been completed.

The tetrahydrofuran solution was cooled (0°) and stirred as 10 ml of H_2O was added slowly. To the cooled solution was added 6 g (0.15 mol) of NaOH in 50 ml of H_2O. During the next half hour, 50 ml of 30% H_2O_2 was added dropwise. The resulting mixture was stirred at room temperature for 1 hr, heated at reflux for 1 hr, cooled, and extracted four times with ether. The combined organic portions were dried ($MgSO_4$), filtered, and distilled to give 4.6 g (76%) of the labeled cyclohexanol, bp 80–90° (25–35 mm).

Cyclohexene-*1,3,3-d*$_3$ oxide was prepared by treatment of cyclohexene-*1,3,3-d*$_3$ with *m*-chloroperoxybenzoic acid (Aldrich Chemical Co.).[14]

Cyclohexanol-*2,2,6-d*$_3$ (1 H cis to 6 H) and cyclohexanol-*1,3,3-d*$_3$ were obtained by treating cyclohexene-*1,3,3-d*$_3$ oxide with $LiAlH_4$.[14]

Cyclohexanol-*1-d* was prepared by the reduction of cyclohexanone with lithium aluminum deuteride[14] in 88% yield: bp 80° (25 mm); nmr (CS_2) δ 1.5 (broad m, 10, CH_2), 4.2 (s, 1, OH). The resonance at δ 4.2 disappeared when the sample was shaken with D_2O.

Cyclohexene-*1-d* was synthesized by conversion of the alcohol to the tosylate and treatment of the latter compound with 2,6-lutidine:[14] nmr (CS_2) δ 1.6 (m, 4, nonallylic CH_2), 2.0 (m, 4, allylic CH_2), 5.6 (m, 1, alkenic); molecular weight, parent ion at *m/e* 83.

Cyclohexyl Acetate. Various deuterated modifications of this material were obtained by treatment of the corresponding alcohols with acetic anhydride.[14]

Cyclohexyl Formate. To 50 ml (1.34 mol) of formic acid was added 5 g (0.06 mol) of cyclohexene, and about 0.05 g of *p*-toluenesulfonic acid monohydrate. This solution was stirred and heated at 50° for 19 hr, after which time it was worked up in the manner used for the formolyses (see below); nmr (CCl_4) δ 1.5 (broad m, 10, CH_2), 4.8 (m, 1, CH), 7.9 (s, 1, CHO).

Cyclohexyl trifluoroacetate was prepared from cyclohexanol and trifluoroacetic anhydride (Aldrich Chemical Co.) in a manner analogous to that used for the acetate.[14]

Acetolyses. Acetic acid was refluxed for 24 hr with enough acetic anhydride to react with all the H_2O present and distilled (118°) from CrO_3. Cyclohexyl tosylate (1.25 g, 0.005 mol) and potassium acetate (0.55 g, 0.0056 mol) were dissolved in 48 ml of acetic acid containing 2 ml of acetic anhydride. This solution (0.1 *M* in tosylate) was stirred at 95° for about 20 hr.

Formolyses. Formic acid was freshly distilled (101°) from boron trioxide, and sodium formate was dried in an oven at 130° for 2 hr. Cyclohexyl tosylate (1.25 g, 0.005 mol) and sodium formate (0.38 g, 0.0056 mol) were dissolved in 50 ml of formic acid. This solution (0.1 *M* in tosylate) was stirred at room temperature for 30 hr.

Trifluoroacetolyses. Cyclohexyl tosylate (1.25 g, 0.005 mol) and sodium trifluoroacetate (0.75 g, 0.0055 mol) were dissolved in 18 ml of freshly distilled (71°) trifluoroacetic acid containing 2 ml of

(12) It should be pointed out that interpretation of the α and β kinetic isotope effects[2b,4] is hopeless unless all the products are generated from pathways that diverge after a common rate-determining step. If elimination, direct substitution, and rearrangement were wholly independent processes involving competing pathways, the isotope effects would be weighted averages of dubious significance. We feel that the data are most easily interpreted in terms of a common rate-determining step, but our results do not demand it.

(13) We thank Dr. C. E. Mixan for recording the low-temperature spectra and Dr. L. Raphaelian for recording the mass spectra.

(14) Details of commonly used procedures are omitted. They are described, however, by G. J. Putz, Ph.D. Dissertation, Northwestern University, 1973.

its anhydride. This solution (0.25 M in tosylate) was stirred at room temperature for 35 min. Crude kinetics of the solvolysis reaction were obtained by monitoring the growth of product peaks (the methyl group in the tosylate anion) in the nmr spectrum.

Deuteriotrifluoroacetic acid was prepared by treating freshly distilled (39°) trifluoroacetic anhydride with an excess of D_2O. The acid was then distilled (71°) and the solvolysis solutions were prepared as with the undeuterated acid.

Isolation and Characterization of Solvolysis Products. Upon completion of the solvolysis reaction, the solution was cooled and the contents of the flask rinsed with ether and water into a stirred solution of 10% excess (based on the solvolysis solvent) NaOH in 150 ml of ice and H_2O. The aqueous solution was extracted twice with 50-ml portions of ether, and the combined organic portions were dried over K_2CO_3 and $MgSO_4$. Analytical vapor phase chromatography was performed on the filtered ether solutions. Equation 1, in which F_1 and F_2 are the correction factors for the sensitivity of the compounds to thermal detection and the concentrations are relative, was used to calculate the product ratios. The correction factors were determined on each analysis from a standard solution. Isolation of products was accomplished by concentrating the solution by distillation of the ether through a 20-cm vacuum-jacketed column packed with glass helices, with the oil bath temperature less than 43°. The residue was purified by preparative vapor phase chromatography.

$$\frac{\text{cyclohexene area}}{[\text{cyclohexene}]} = F_1\frac{\text{ester area}}{[\text{ester}]} = F_2\frac{\text{alcohol area}}{[\text{alcohol}]} \quad (1)$$

Product Stability. To the normal acetic or trifluoroacetic acid solvent systems (containing the buffer) was added 0.93 g (0.005 mol) of *p*-toluenesulfonic acid monohydrate and an extra milliliter of anhydride. For formic acid studies, the *p*-toluenesulfonic acid monohydrate was dissolved in benzene, the water was removed by azeotropic distillation (78°), and the benzene was evaporated. The dried acid (0.86 g, 0.005 mol) was then added to the buffered formic acid solvent. The product to be tested (0.3 g, 0.004 mol of cyclohexene or 0.0015 mol of ester) was added, and the solution was subjected to normal solvolysis and work-up conditions.

Solvolytic Behavior of 7,7-Dimethoxybicyclo[2.2.1]hept-2-yl Tosylates[1]

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Abstract: The solvolysis of *exo*- and *endo*-7,7-dimethoxybicyclo[2.2.1]hept-2-yl tosylates has been studied in acetic acid buffered with sodium acetate and in absolute ethanol buffered with *syn*-dimethylurea (DMU). Whereas the exo isomer appeared to solvolyze in a straightforward manner, the endo isomer underwent ionization with MeO-4 neighboring group participation. As a result, the *exo*- and *endo*-7,7-dimethoxybicyclo[2.2.1]hept-2-yl tosylates gave different products on acetolysis and on ethanolysis. The implications of these results on bicyclic cation theory are discussed.

The 2-norbornyl cation remains as one of the more discussed subjects in organic chemistry. Even after extensive amounts of investigation, the nature of this cation is not agreed upon.[3] Numerous approaches have been taken to resolve the question of whether the 2-norbornyl cation is a classical ion with its charge localized on a particular carbon or a nonclassical ion with a highly delocalized electronic structure. Rate studies, product studies, spectroscopic measurements, and theoretical calculations have all been utilized in attempts to obtain the definitive answer. The most effort has been devoted to kinetic and product studies. The emphasis on these approaches is probably a consequence of the historical reasons for the initial suggestion of the existence of the nonclassical norbornyl cation.[4,5] In most of the early studies, attention was focused on the effects of carbonium ion stabilizing groups such as alkyl and aryl moieties.[3] As part of our general interest in this area, we carried out several studies of the effect of electron-withdrawing substituents on both the rates of solvolysis and product compositions obtained from *exo*- and *endo*-bicyclo[2.2.1]heptyl tosylates.[1,6-8] We now wish to present the details of our study of the solvolytic behavior of *exo*- and *endo*-7,7-dimethoxybicyclo[2.2.1]hept-2-yl tosylate.

Synthesis. *exo*-7,7-Dimethoxybicyclo[2.2.1]heptan-

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