# Trifluoroacetolysis of Optically Active 2-Butyl Tosylate

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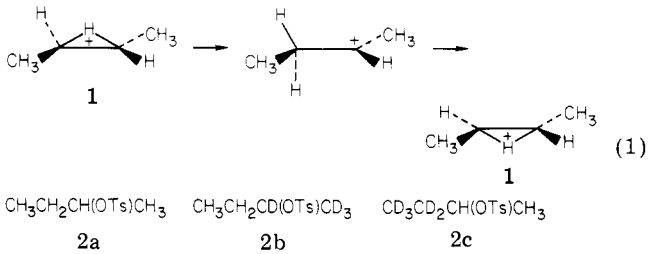
*Received April 26, 1983*

The trifluoroacetolysis of optically active 2-butyl tosylate proceeds with 13% net inversion at 37 °C. The respective rates of loss of optical activity, solvolysis, and racemization of starting tosylate are 8.2, 7.2, and 2.7 $\times 10^{-4}$. The data indicate that the solvolysis occurs with about 40% inversion after correction for racemization of tosylate. This is the first reported example of a solvolysis of a simple secondary alkyl substrate that does not occur with complete inversion. The mechanism for this reaction is proposed to involve attack by solvent both upon an intermediate where the leaving group determines the stereochemistry of the reaction and upon free solvated hydrogen-bridged 2-butyl cation. Racemization is thought to occur by elimination/readdition of HOTs in a side reaction that is not part of the solvolysis reaction path. It is unlikely that the hydrogen bridge is strong enough to determine the stereochemical course of the solvolysis reaction. Trifluoroacetolyses of optically active and/or isotopically labeled substrates should be useful probes for the study of the intricate details of nucleophilic substitution reaction paths.

The 2-butyl cation is an intermediate of considerable interest since, except for the unstable ethyl cation, it is the simplest alkyl cation that is capable of assuming a symmetrically hydrogen-bridged structure, 1. During the past




few years, there have been several reports of both experimental (the trifluoroacetolysis of 1,1,1,2-tetradeuterio-2-butyl tosylate, **2b**[2], isotopically perturbed NMR studies in superacid solution[3]) and theoretical (CEPA ab initio and MINDO/3 calculations[4]) studies that support 1 as the structure of this species. All of these studies, however, suggest that the energy difference between the bridged and open structures is very small.

The stereochemistry of nucleophilic substitution has often been used as an experimental probe for the existence of bridged intermediates and neighboring-group participation. However, such tests really indicate whether or not racemization of the cationic intermediate competes favorably with trapping by solvent or another nucleophile. The stereochemical consequences of any optically active bridged intermediate depend upon the activation barrier for conversion to its enantiomer. These barriers should be much higher for such common bridged ions as phenonium or bromonium than for 1. Since the "open" cation can be the transition state for racemization of optically active 1 (reaction 1), the barrier for inversion of free 1 must be no greater than the energy difference between the bridged and open 2-butyl cations. In this case, racemization of the bridged cation might compete with trapping by solvent to form product, thereby rendering the stereochemical test inconclusive.

Aside from racemization of the bridged ion, 1, there are two other possible routes for formation of racemized products. As the *cis*-bridged cation contains a plane of symmetry, any reaction proceeding *via* this species would necessarily be racemized. We estimate the difference in energy between the *cis* and *trans* ions to be about the same as that between the *cis*- and *trans*-2-butene, or 1 kcal/mol. To the extent that some elimination followed by readdition of HOTs occurs in the trifluoroacetolysis reaction mixture, racemization of starting material (eventually leading to racemized product) should be observed.

Despite the remote likelihood of observing complete stereoselectivity in this case, it is of interest to determine whether the trifluoroacetolysis of optically active 2-butyl tosylate, **2a**, proceeds with net inversion (like all known simple solvolyses of secondary alkyl substrates that do not involve neighboring group participation, multiple inversions, benzylic allylic, or other special stabilization[5]) or net retention (as in solvolyses proceeding *via* aryl-bridged cations). Net inversion would indicate that the solvent attack occurs on a cationic intermediate in which the leaving group is still associated with, and still responsible for stereochemical control of the 2-butyl cation. This situation would obtain if removing the leaving group requires more energy than needed to open the bridge. Net retention would be expected from a free bridged ion, but only to the extent that trapping the cation competes favorably with the racemization process (reaction 1). The amount of the net retention or inversion observable will, of course, be reduced to the extent that either *cis*-bridged intermediates and elimination/readdition compete with the substitution process.

Prior to this work and that of Tidwell,[6] there have been no reports of successful attempts to measure the stereochemistry of the trifluoroacetolyses of simple secondary alkyl substrates. Notably, trifluoroacetolysis of 2,2,6-trideuteriocyclohexyl tosylate yielded product with too much scrambling of the isotopic label for Lambert to determine the stereochemistry of the substitution reaction.[5]

In this context, we have investigated the stereochemistry of the trifluoroacetolysis of **2a**. The report of similar work by Tidwell et al.[6] has prompted us to communicate our results at this time.

(1) National Science Foundation undergraduate research participant, 1981.

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0022-3263/83/1948-4524$01.50/0 

## Results

Optically active **2a** was trifluoroacetolysized at 37 °C. The rates of loss of optical activity ($k_\alpha$) were measured by using a digital polarimeter at 578 nm. Readings at other wavelengths were consistent when available. The formation of a slight coloration as the reaction progressed rendered the monitoring of the rotation at shorter wavelengths difficult. Racemization of unreacted **2a** was measured by quenching samples of the reaction mixture by pouring into ice water, neutralizing, extracting, and evaporating off the ether and trifluoroacetate product under high vacuum. Samples of recovered **2a** were pure by NMR. Their rotations were measured in $CCl_4$. The rotation of 2-butyl trifluoroacetate (**3**) product after at least 10 half-lives was compared with **3** that was prepared by a stereoselective process from the same sample of optically active 2-butanol as the starting **2a**. The specific and molecular rotations of **2a** in trifluoroacetic acid (TFA) were obtained by extrapolating the plot of rotation vs. time to the time of mixing.

The **3** formed from solvolysis of *R*-(−)-**2a** was observed to be *S*-(+) with $[\alpha]^{TFA}_{578}$ 1.62°. This result corresponds to a 13% net inversion of configuration $[\alpha]^{TFA}_{578}$ = 11.8° for pure **3**. The rates of the processes measured are collected and compared with others reported[2] in the table. The interpretation and measurement of $k_\alpha$ are subject to some error as the observed rotation at any time is the sum of the contributions of **2a** and **3**. Fortunately, the molecular rotations differ by only approximately 10% (−22.2° and −20.1°, respectively). The $k_\alpha$ reported here is the rate at which the rotation goes to zero (not the infinity reading).

## Discussion

In order to obtain the stereospecificity of the substitution (reaction 2) it is necessary to account for the race-

$$\underset{\mathbf{2}}{\text{2-butyl tosylate}} \xrightarrow{\text{TFA}} \underset{\mathbf{3}}{\text{2-butyl trifluoroacetate}} \quad (2)$$

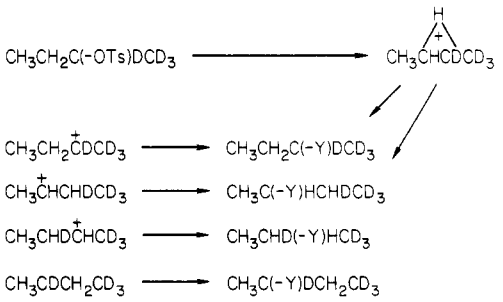
$$\underset{\mathbf{2a}}{\text{2-butyl tosylate (active)}} \rightarrow \underset{\mathbf{2a}}{\text{2-butyl tosylate (racemic)}} \quad (3)$$

$$k_\alpha = Fk_{solv}\left(\frac{k_{solv}}{k_{solv} + k_{rac}}\right) + k_{rac}\left(\frac{k_{rac}}{k_{solv} + k_{rac}}\right) \quad (4)$$

mization of starting **2** (reaction 3). Equation 4 gives the relationship between $k_\alpha$, $k_{solv}$, and $k_{rac}$, where $F$ is a measure of the stereospecificity of the substitution reaction ($F$ = 0) implies retention, $F$ = 1, racemization, $F$ = 2, inversion, etc.). The quantities in brackets correspond to the fraction of the optically active **2a** that loses activity *via* each of the two processes. Solving for $F$ in eq 4 yields a value of 1.4, or the substitution process occurs with about 40% inversion of configuration. As all the errors in the measured $k$'s are accumulated in this result, some caution should be used in interpreting this result quantitatively. A 10% error in $k_\alpha$ will result in an error of 0.15 in $F$ or a 35% error in the per cent inversion.

Since a portion of the substitution reaction will go through the *cis* cationic intermediate, the observed per cent inversion will be less than the per cent attack from the side opposite the leaving group. If the 1 kcal/mol difference in energy estimated above holds for the activation energies for reaction *via* the *cis* and *trans* bridged ions, 17% of the solvolysis reaction should occur *via* the *cis* ion. The reaction that proceeds through the *trans* ion must occur with approximately 50% inversion, after correction for that part of the reaction path that proceeds *via cis* ion.

Scheme I[a]




[a] Y = trifluoroacetate.

The simplest interpretation of the stereochemical data, that the reaction proceeds partly *via* a free open carbocation to give racemization and partly *via* an intermediate (perhaps an ion pair) to give inversion, is inconsistent with the deuterium labeling experiments that we have previosly reported.[2] In particular, a free carbocation formed from **2b** should form only one product if it did not undergo 3,2-hydrogen shifts and a mixture of four products if it undergoes extensive shifts. We have observed that only two major products are formed in a 1:1 ratio (see Scheme I).

Burnett has recently reported that $^{18}O$ scrambling occurs in the solvolyses of 2-propyl and 2-adamantyl benzenesulfonates.[11] Scrambling of this kind can occur by elimination/addition (where possible) as well as *via* 1,3-sigmatropic shift of the alkyl group from one oxygen to another. Interestingly, 1,3-shifts are allowed with retention (as well as inversion) of configuration for the case of an alkyl group migrating on an $ArSO_3$ system. Since the $ArSO_3$ group has an effective 3-fold axis of symmetry, the HOMO's are a degenerate pair, one of which has two oxygen lone pairs of the same sign. The report of $^{18}O$ scrambling in the case of 2-adamantyl benzenesulfonate, where inversion of the alkyl group is extremely unlikely, is consistent with this idea. There is no precedent for the suggestion[6] that simple alkyl cations can invert in ion pairs.

An interpretation of the present results that is in agreement with our previous observations is that the solvolysis proceeds *via* a mixture of solvent attack on free bridged cation and some hydrogen-bridged intermediate where the leaving group, rather than the bridging hydrogen, is stereochemically determinant. However, the data do not allow us to determine the extent of retention or racemization that occurs from the bridged ion, **1**. Using the estimate that the fraction of the product formed from both the *trans* H-bridged intermediates is 50% inverted, one can place limits on the amount of the solvolysis that goes through the free, solvated intermediate and the intermediate still interacting with the leaving group. If we assume that **1** forms product with complete retention of configuration (in this case racemization of **1** is slow with respect to trapping by solvent) roughly 25% of the solvolysis must go through a free bridged ion and 75% through an intermediate that yields inverted product. On the other hand, if we assume that **1** forms product with complete racemization (that is, racemization by reaction 1 is fast with respect to trapping by solvent), then roughly 50% of the solvolysis must occur *via* free **1**.

The ratio of the rates of solvolysis of **2a** to **2b** (2.9) is what one would expect for limiting secondary $\alpha$ and $\beta$ deuterium isotope effects,[7] while the ratio of the rates of **2a**/**2c** (3.0) is consistent with one limiting secondary

(7) Shiner, V. J., Jr.; Dowd, W. *J. Am. Chem. Soc.* **1971**, *93*, 1029.

deuterium isotope effect (1.2) and one isotope effect due to a participating deuterium (2.5).[8] Large values for secondary deuterium isotope effects have been interpreted as being indicative of solvolyses where the dissociation of the solvent separated ion pair (or anion–cation stabilized intermediate[9]) is rate limiting. This is, also, in agreement with expectation for a reaction where a significant fraction of the product is formed from a free carbocation.

The rate of trapping of a fully solvated carbocation can be no greater than the rate of diffusion, as the stereochemical influence of the leaving group will not cease until it has diffused away from the cation. If a free, solvated cation is formed, the rate of trapping of this cation must be significantly faster than the racemization process (reaction 1), if the hydrogen bridge in 1 is to be stereochemically determinant. The energy difference between the bridged and "classical" 2-butyl cations have been estimated to be 4–8 kcal/mol by CEPA ab initio and MINDO/3 molecular orbital calculations.[4] This difference might be lowered somewhat by the presence of even a very weakly nucleophilic solvent, such as TFA. Assuming a preexponential factor of $10^{13}$, the predicted rate constant for the lowest of the calculated barriers (4 kcal/mol) is $1 \times 10^{10}$, which is similar to the rate for diffusion-controlled reactions.

We have previously suggested that TFA solvates cations by means of the electrostatic interaction of the trifluoromethyl group with the cationic site.[10] Since such an interaction cannot lead directly to bonding, it will occur at longer solvent–cation distances than expected for more nucleophilic solvents, such as acetic acid. Since the TFA molecule would have to turn around, and perhaps break hydrogen bonds to another TFA molecule before it could react with the carbocation, a several kcal/mol barrier for carbocation trapping is not unreasonable. On this basis, competition between racemization and trapping of the bridged cation, 1, to form product seems to be a viable possibility.

The stereochemical behavior of the trifluoroacetolysis of **2a**, as well as the deuterium labeling studies of **2b** and **2c** previously reported,[2] are all consistent with the rate of trapping of free carbocation, 1, occurring at approximately the same rate or faster than racemization by reaction 1. If reaction 1 were much faster than the trapping of 1, complete scrambling of the hydrogen isotopes of carbons 2 and 3 of **2b** should have been observed. If the attack of TFA on solvated 1 were much faster than racemization, than retention of configuration *for that fraction of the reaction that involved the intermediacy of solvated cation* should occur, a possibility that cannot be ruled out (see above).

As we have already noted, all uncomplicated nucleophilic substitution reactions on secondary alkyl substrates proceed with complete inversion. In at least one case, the acetolysis of 2,2,6-trideuteriocyclohexyl tosylate, the acetate product has been shown to be formed with inversion[5] by attack on the solvent-separated ion pair (or anion–cation stabilized intermediate).[12] MINDO/3 calculations, although they predict the cyclohexyl cation to also be hydrogen-bridged, suggest the open cyclohexyl cation to be almost planar, with the chair and boat forms within 1 kcal/mol of each other in energy.[13] Ring conformation should not, therefore, impede ion pairs of the open cyclohexyl cation from undergoing inversion at the cationic carbon, yet none is observed.[5,12]

Table I. Rates of Various Processes

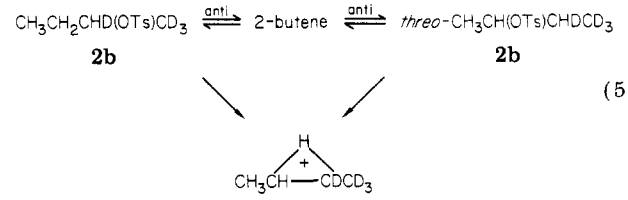
| processes | $10^4k$, $s^{-1}$ |
|---|---|
| trifluoroacetolysis of **2a** ($k_{solv}$) | 7.2 |
| trifluoroacetolysis of **2b** | 2.9[a] |
| trifluoroacetolysis of **2c** | 2.4[a] |
| loss of optical activity ($k_\alpha$) | 8.2 |
| loss of optical activity with 0.18 M NaOTFA | 7.7 |
| racemization of **2** ($k_{rac}$) | 2.7 |

[a] Reference 2.

The rate of loss of optical activity, $k_\alpha$, decreases slightly upon addition of sodium trifluoroacetate (NaOTFA) to the reaction mixture (see Table I). As the overall net stereochemistry observed is inversion, a reduction in $k_\alpha$ must be due to a relative increase in those processes that lead to either retention or racemization of some combination of them. The trifluoroacetate anion ($OTFA^-$) can act both as a nucleophile and/or a base. Consequently, it may increase the net amount of retention that results from the *trans* bridged ion, **1a**, by increasing the rate of trapping (nucleophile), or it may increase the rate of elimination from the intermediate that leads to inverted product, thereby increasing the amount of racemization relative to inversion (base). We have previously reported that NaOTFA increases the steady state concentration of 2-butene observed during the trifluoroacetolysis of **2a**,[2] which is in accord with the latter suggestion. However, the former cannot be eliminated as a possibility by the present evidence.

The rate of racemization of starting material is 38% of that for solvolysis (see Table I). The mechanism for racemization may be either internal return from a *cis* H-bridged intermediate (ion pair, anion-stabilized or anion–cation-stabilized intermediate[9]) to rearranged tosylate, where the bridging H has undergone a 3,2-shift while the OTs has undergone a 2,3-shift, or elimination followed by readdition of HOTs. Internal return from a *trans* H-bridged intermediate would not lead to racemization. Previous studies on the trifluoroacetolysis of **2b** have indicated that internal return with rearrangement occurs at a rate similar to that of solvolysis.[2]

Although the addition of HOTs to 2-butene in TFA is very fast, the addition of TFA is slow compared to the rate of trifluoroacetolysis of **2a**.[2] Therefore, elimination/readdition of HOTs may occur to a substantial extent, but it is a process that cannot be part of the reaction path for the solvolysis reaction since addition of TFA is slower than the latter reaction. If the elimination of HOTs from **2b** be stereospecifically *anti*, either **2b** or **2b′** would be formed (reaction 5) since the readdition must have the same ste-




(5)

reospecificity according to the principle of microscopic reversibility. Both **2b** and **2b′** will form the same *trans*-

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bridged carbocation upon loss of OTs. This process is operationally equivalent to the rearrangement of **2b** via a *trans*-bridged ion as proposed previously. Formation of the *erythro*-**2b'**, which can form *trans* deuterium-bridged carbocations, can occur only if elimination/readdition be *syn* or nonstereospecific. The results previously reported for the trifluoroacetolysis of **2a** preclude the formation of any appreciable amount of deuterium-bridged carbocation.[2]

Since the trifluoroacetolyses of simple secondary alkyl substrates seem to proceed by at least two paths, one involving a free, solvated cation and the other an intermediate that is still associated with the leaving group, the further study of optically active alkyl substrates capable of hydrogen bridging can be a useful probe of the intricate details of the intermediates involved during nucleophilic substitutions, particularly when combined with isotopic labeling studies.

## Experimental Section

**(*R*)-(−)-2-Butyl Tosylate (2a).** (*R*)-(−)-2-Butanol (Aldrich) was reacted with purified[13] toluenesulfonyl chloride according to an established procedure.[14] The 2-butyl tosylate obtained had specific rotation $[\alpha]^{37}\,^{\circ}C_{CCl_4}$ −11.04 at 578 nm.

**2-Butyl Trifluoroacetate (3).** Trifluoroacetic anhydride (8 mL) was added dropwise to a solution of (*R*)-(−)-2-butanol in 60 mL dry pyridine over 15 min at 0 °C.[16] Upon completion of the reaction, the mixture was allowed to come to room temperature. It was then poured into 300 mL of ice water and extracted with ether. The ether solution was washed with 10% HCl, 10% $NaHCO_3$, and water and then dried over anhydrous $MgSO_4$. The 2-butyl trifluoroacetate was recovered upon evaporation of the ether at reduced pressure. Specific rotation $[\alpha]^{37}\,^{\circ}C_{TFA}$ −13.03 at 578 nm.

**Trifluoroacetic Acid.** Trifluoroacetic acid (Aldrich) for all solvolyses was freshly distilled. A small amount of trifluoroacetic anhydride (1%) was added to assure dryness.

Optical rotations were made on solutions thermostatted at 37 °C by using a Perkin-Elmer Model 141 digital polarimeter. For the kinetic studies polarimeter readings at 578 nm were taken approximately 1 min apart for at least two half-lives. Infinity readings were taken after at least 10 half-lives and again after 24 h. No significant changes in optical rotation were observed after 10 half-lives.

**Acknowledgment.** This work was supported in part by PSC-BHE Grant No. 13361.

**Registry No. 2a**, 61530-30-1; **3**, 66585-35-1.

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# Stereochemistry of Trifluoroacetolysis of Optically Active 2-Butyl Tosylate. A Test for Hydrogen Bridging

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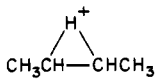
*Received May 10, 1983*

Trifluoroacetolysis of (*R*)-(−)-2-butyl tosylate at 25 °C gives 2-butyl trifluoroacetate with 7 ± 1% net inversion. The ratio of the polarimetric and spectrophotometric rate constants is 1.55, and this decreases to 1.05 in the presence of 0.125 M $NaO_2CCF_3$. These results are most simply and plausibly interpreted in terms of formation of an ion pair consisting of an open 2-butyl cation and a tosylate anion which gives racemized tosylate by ion-pair return and by elimination/readdition, with competitive nucleophilic solvent attack with a small overall preference for substitution on the side opposite the anion. A published proposal based on deuterium labeling studies that a hydrogen-bridged butyl cation is the predominant intermediate in this reaction does not give a simple prediction of these results.

It has recently been reported[1] that the rates and products of the solvolysis in trifluoroacetic acid (TFA) of $CH_3CH_2CH(OTs)CH_3$ (**1**), $CH_3CH_2CD(OTs)CD_3$ (**2**), and $CD_3CD_2CH(OTs)CH_3$ (**3**) "are consistent with the intermediacy of a hydrogen-bridged 2-butyl cation" and led the authors "to conclude that a bridged ion . . . is the predominant intermediate." The proposed structure of the bridged ion from **1** can be represented as **4**.



**4**

This report has already attracted notice in the literature.[2] Further, because there is widespread interest in the possibility of hydrogen bridging in solvolysis reactions[3a,b] and alkene protonations,[3c-e] as well as a continuing interest in the details of solvolysis processes,[4] further study of the solvolysis of such simple secondary systems appeared desireable. We have now studied the reactivity of optically active 2-butyl and 2-octyl tosylates, which provide an independent insight into the behavior of such systems.

A concise statement of the stereochemical consequences expected for different mechanisms of substitution at a

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