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# Nucleophilic and electrophilic solvent effects in the solvolysis of alkyl tosylates

Michael T. Lane  
*San Jose State University*

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alkyl tosylates**

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San Jose State University, 1992

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Nucleophilic and Electrophilic Solvent Effects  
in the Solvolysis of Alkyl Tosylates

A Thesis

Presented to

The Faculty of the Department of Chemistry

San Jose State University

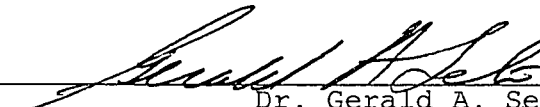
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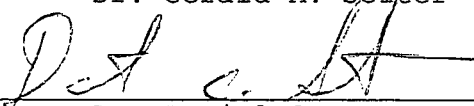
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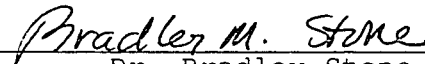
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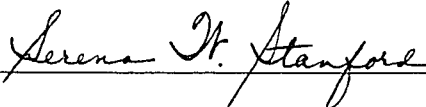
  
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ABSTRACT

NUCLEOPHILIC AND ELECTROPHILIC SOLVENT EFFECTS  
IN THE SOLVOLYSIS OF ALKYL TOSYLATES

by Michael T. Lane

Product studies for 1-adamantyl tosylate (**1-Ad-OTs**) and 2-adamantyl tosylate (**2-Ad-OTs**) in ethanol and 2,2,2-trifluoroethanol (TFE) solvent mixtures suggest different mechanisms for reactions at the frontside and backside of the reacting center. The attempted synthesis of 1-methyl-4-adamantyl tosylate, which would afford different products from reaction at opposite faces of the reacting center, is described. *trans*-4-*t*-Butylcyclohexyl tosylate (***trans*-4-OTs**) was prepared. The solvolysis rates and the product distributions were measured in ethanol/TFE media. The rates and product distributions are inconsistent with those expected from classical theories<sup>1,2</sup> of solvolysis mechanisms. The first-order rates of formation of the ether products from ***trans*-4-OTs** solvolysis in ethanol/TFE media are nonlinear with respect to solvent mole fraction. The results support the proposal that the solvolysis mechanism differs for frontside and backside reactions. The effect of solvent in the solvolysis of 1-bicyclo[2,2,1]heptan carbinyl tosylate was also investigated. The results of this study also support a mechanism in which the solvent is intimately involved in the reaction mechanism.



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## Introduction

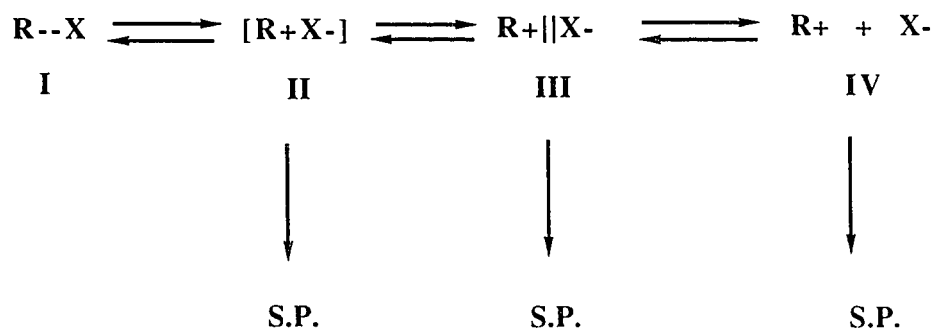
Hughes and Ingold originally classified the mechanisms of nucleophilic substitution reactions according to the molecularity of the reaction (i.e.,  $S_N1$  and  $S_N2$ ).<sup>3</sup> Their proposed mechanisms were generic in that they were not intended to be applied exclusively to solvolysis reactions. Solvolysis reactions are generally defined as reactions in which the solvent is a reactant and is incorporated into the reacting substrate. The rates of these reactions are very sensitive to the nature of the solvent. For example, it has been found that the rate of solvolysis of **1-Ad-OTs** increases 10,000 fold while progressing from ethanol to TFE.<sup>4</sup>

Solvolytic displacement reactions have been a topic of considerable debate amongst physical organic chemists for well over four decades.  $S_N2$  reactions, where little or no charge develops on the electrophilic carbon, are well characterized. The  $S_N2$  mechanism is not vigorously debated. However,  $S_N1$  reactions, in which catenoid intermediates are invoked, are not as well understood. Between the original mechanistic definition of  $S_N1$  and  $S_N2$  solvolyses there is a sharp distinction, no nucleophilic assistance by solvent in the rate determining step of the former but full nucleophilic participation in the latter. It has long been recognized that such a sharp distinction cannot in fact be made.

The Winstein Ion Pair Scheme<sup>5</sup> (Scheme 1) is the most often used and widely accepted mechanistic framework utilized

to discuss these reactions. According to Winstein's interpretation, the ionization of alkyl halides and arenesulfonates proceeds through a series of increasingly more dissociated intermediates: The existence of these

**Scheme 1.** Winstein Ion Pair Scheme



S.P., solvolysis product.

intermediates as discrete entities, as opposed to a continuous spectrum of increasingly dissociated ions, has been the focus of many authors' attention. Further discussions will not be addressed here, but may be found elsewhere.<sup>6,7</sup> In relation to Scheme 1, it is useful to

define<sup>8</sup> some terms with regard to the reverse reactions that regenerate covalently bonded substrate:

1. Internal Return--Collapse of intimate ion pair (**II**->**I**).
2. External Ion Pair Return--Collapse of the solvent separated ion pair (**III**->**I**) or (**IV**->**I**).

Within the context of this scheme, reaction with solvent

may occur with any of these species. The actual species that are kinetically significant depend greatly on both the nature of the solvent and the reacting substrate. It is implied that as the stability of the  $R^+$  entity is increased, the site of solvent attack is shifted to the right in the scheme.

Limiting  $S_N1$  has been introduced by Streitweiser<sup>9</sup> to mean reactions that proceed through completely dissociated ions and whose rate is unaffected by the nucleophilicity of the solvent. Although the limiting  $S_N1$  mechanism is followed by some substitutions, a greater number of displacements that have a catenoid intermediate proceed by a mechanism that is modified in one or both of the following ways:<sup>10</sup> (1) The solvent provides nucleophilic assistance to ionization; (2) The nucleophile attacks an ion pair intermediate rather than a free carbocation. The Winstein Ion Pair Scheme does much to explain the mechanistic nature of a variety of solvolysis reactions. However, the role of solvent is rarely considered, even though the orientation of solvent molecules with respect to the reacting substrate is used as a means of distinguishing ion pair intermediates.

Historically, solvent effects, solvolysis rates, and mechanisms have been treated quantitatively within the context of the Grunwald-Winstein<sup>2</sup>  $\rho$  scale (equation 1).

$$\text{Log } k/k_0 = \rho Y \quad (1)$$

In this linear free energy relationship, the rate of

solvolysis for the standard compound *t*-butyl chloride in 80% aqueous ethanol is  $k_0$ . The assumed mechanism of reaction for *t*-butyl chloride was complete bond cleavage to give free ions, followed by reaction of solvent and cation leading to product. The substrates' sensitivity to ionizing power ( $m$ ) was defined as one for this compound. The solvolysis rates ( $k$ ) for a variety of solvents were measured and used to define the ionizing power ( $Y$ ) for each of these solvents. For  $Y$  to be a true measure of the ionizing ability of a solvent, the rate determining step in the solvolysis reaction must be complete bond cleavage to give a freely solvated *t*-butyl cation and chloride anion before any nucleophilic solvent assistance occurs. If this is not the case and the rate determining step is diffusion to either ion Pair **II** or **III**, then the effect of solvent is somewhat less certain. The measured  $Y$  value would be a composite of the solvent's ability to support charge, its nucleophilicity, acidity, and a number of other factors. Mechanistic interpretations derived from these  $Y$  values would then be of little value.

There is significant evidence that demonstrates that *t*-butyl chloride undergoes bond cleavage with substantial backside nucleophilic solvent assistance. When comparing the rates of solvolysis of *t*-butyl chloride with the rates of 1-adamantyl chloride, it is observed that the rate of reaction of *t*-butyl chloride is 3000 times faster in ethanol and only 3 times faster in the much less nucleophilic solvent



97% hexafluoroisopropanol.<sup>11,12</sup> The relative increase in the rate for *t*-butyl chloride in ethanol is attributed to nucleophilic assistance to ionization from the backside. This rate enhancement is not possible in 1-adamantyl chloride due to its cage structure, which forbids solvent molecules from approaching the reacting center from the rear. In an attempt to find a more suitable reference substrate, Schleyer<sup>13</sup> proposed and developed a Y scale based on the solvolysis of **2-Ad-OTs**. It was assumed that the beta hydrogens that are *trans* with respect to the tosylate moiety would prohibit backside nucleophilic attack and that internal return in this substrate is not significant. This is equivalent to requiring that ionization to the internal ion pair be rate determining.

Bunnett and Paradisi later refuted this assumption.<sup>14</sup> They subjected <sup>18</sup>O labeled 2-adamantyl benzenesulfonate to partial solvolysis, recovered the starting material, and observed scrambling of the <sup>18</sup>O label. Their work shows that the rate of <sup>18</sup>O equilibration via internal return is at least 3 times faster than the solvolysis reaction. The minimum value of 3 is a consequence of invisible return, i.e., return of the <sup>18</sup>O label to its original position, which is assumed to be at least as likely to occur as return of another oxygen. Bentley and coworkers<sup>15</sup> have argued that the pathway

that leads to oxygen scrambling is not the solvolytic pathway and that 2-adamantyl tosylate is still a suitable compound for defining limiting  $S_N1$ .

Compounds with similar  $m$  values are assumed to have the same sensitivity to "solvent ionizing power." A value of  $m$  near unity indicates a substrate that proceeds through intermediates with a high degree of charge separation. Low  $m$  values near 0.2-0.3 e.g. methyl tosylate and ethyl tosylate indicate  $S_N2$  reactions with little charge separation in the transition state. This treatment becomes very suspect when  $m$  values greater than unity are encountered. Examples of compounds with  $m$  values greater than one are 1-phenylethyl chloride in water/acetic acid ( $m = 1.245$ ) and benzhydryl bromide in dioxane/water ( $m = 1.049$ ).<sup>16</sup> Values of  $m$  derived from solvolysis of these compounds serve little purpose for making mechanistic interpretations. The  $mY$  scale can serve a useful purpose, however. It can be used as a tool for determining relative reaction rates for compounds that solvolyze via similar mechanisms.

It is the purpose of this paper to elucidate, in as much detail as possible, the role of solvent in the solvolysis of some simple secondary and tertiary alkyl sulfonates. The first dilemma to overcome is choosing proper solvents. Ideally one would choose two solvents which differ in only one physical property. Any change in the reaction kinetics or products as a function of composition could then be

attributed directly to that one factor. Two such solvents are almost inconceivable. However, the two alcohols, ethanol and TFE come very close. Some of their key physical properties are given in Table I.<sup>17</sup> Of significance in this

**Table I:** Physical constants for ethanol and TFE

| Solvent                            | Rel. Molec. Volume | Dielectric Constant | Rel. Nucleophil. | Rel. Ionizing | pKa  |
|------------------------------------|--------------------|---------------------|------------------|---------------|------|
| CH <sub>3</sub> CH <sub>2</sub> OH | 1                  | 24.32               | 1000             | 1             | 15.9 |
| CF <sub>3</sub> CH <sub>2</sub> OH | 1.2                | 26.14               | 1                | 3500          | 12.4 |

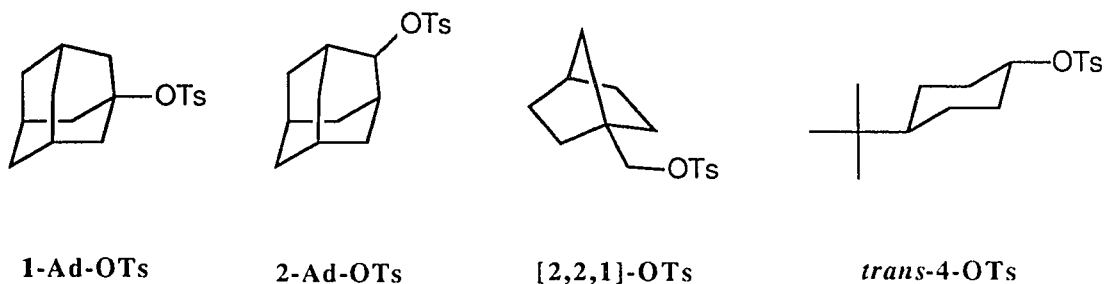
solvent system is the similarity in the dielectric constants and molecular volumes of the two solvents. Some of the other physical properties of mixtures of EtOH and TFE are listed in Table II.<sup>17</sup>

**Table II:** Physical Properties of EtOH and TFE

|                              | X <sub>TFE</sub> |
|------------------------------|------------------|
| B.P. maximum                 | 0.39             |
| Partial Molar Volume maximum | 0.24             |
| Viscosity minimum            | 0.24             |

It has been shown that the mY scale leaves a great deal to be desired when explaining the solvent's role in solvolysis reactions. We have chosen to take a different

route to evaluate the mechanisms of these solvolysis reactions. It was postulated that a detailed study of the reaction products would afford meaningful mechanistic interpretations. The substrates chosen for this study were **1-Ad-OTs**, **2-Ad-OTs**, 1-bicyclo[2,2,1]heptan carbinyl tosylate (**2,2,1-OTs**), and **trans-4-OTs**.



As mentioned earlier, the product studies for **1-Ad-OTs** and **2-Ad-OTs** suggest different mechanisms for reaction at the frontside and backside of the reacting carbon of **2-Ad-OTs**. Unfortunately, displacement of the tosylate moiety from the backside or frontside affords products that are indistinguishable. If either *cis* or *trans* 1-methyl-4-adamantyl tosylate were subjected to solvolysis, it could be determined which products arose from frontside reaction and which arose from backside reaction. It was assumed that the gamma-methyl group would not appreciably perturb the system and therefore would maintain the integrity of the model. The synthesis of 1-methyl-4-adamantanol, however, proved difficult.

The alternative system chosen for study was **trans-4-OTs**. Although this molecule deviates from the 2-adamantyl model, it does function admirably as a substrate

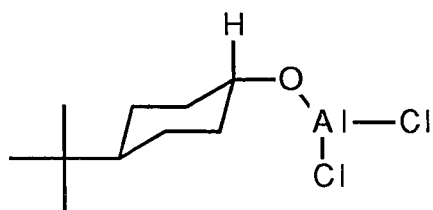
with which to probe frontside and backside reactions. The *t*-butyl group and the tosylate group oriented in the 4-*trans* position relative to one another insure that the molecule is locked in the diequatorial conformation. The high-field NMR spectrum has confirmed this molecular conformation as the ground state. With ***trans-4-OTs*** as the model, the two products of retained or inverted configuration can be distinguished by virtue of their epimeric relationship to the *t*-butyl group.

## Results and Discussion

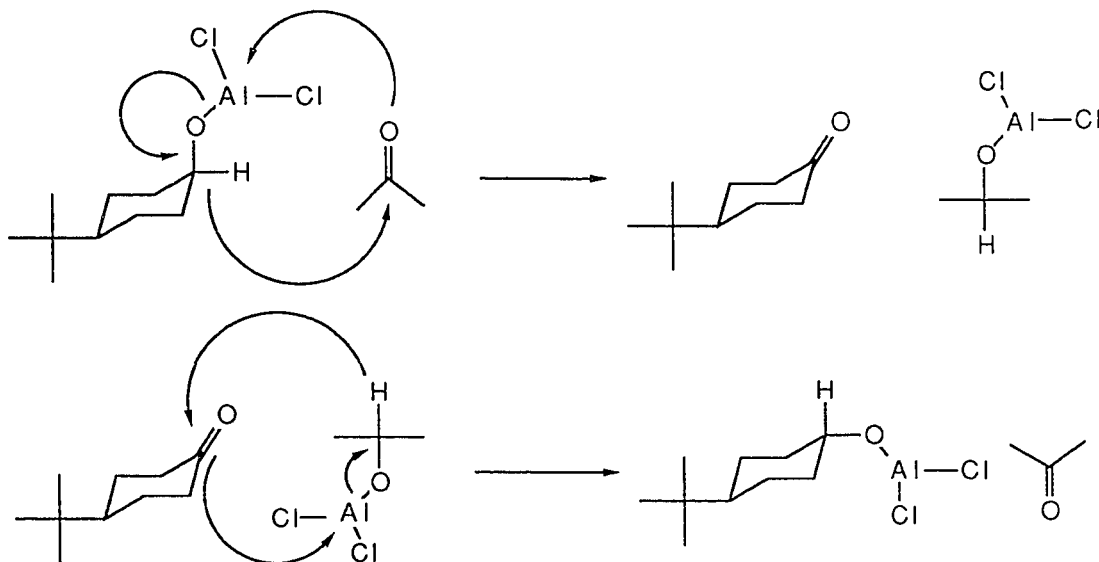
### Results of synthetic efforts

1-Bicyclo[2,2,1]heptan carbonyl tosylate and **2-Ad-OTs** were prepared by standard methods<sup>18</sup> from the corresponding alcohols and toluenesulfonyl chloride. Infrared spectra were consistent with the published data.<sup>4</sup> 1-Adamantyl tosylate was prepared from 1-adamantanol as described by Kevill.<sup>17</sup> *trans-4-t*-Butylcyclohexyl tosylate was prepared from *trans-4-t*-butylcyclohexyl alcohol. The *trans* alcohol was obtained by equilibration of a *cis/trans* mixture of alcohols with one hydride equivalent of **LAH**, and 3/4 aluminum equivalent of AlCl<sub>3</sub> and a catalytic amount of acetone. After 3 iterations, the *trans* alcohol was obtained in 98% epimeric purity by GC. Attempts to obtain a higher degree of purity were unsuccessful. Steric interaction parameters for an axial vs. an equatorial *t*-butyl group indicate that 98.5:1.5.

is the equilibrium ratio for the *trans*:*cis* isomers.<sup>19</sup> It appears that upon addition of the **LAH** and aluminum chloride, an alkoxy aluminate complex is formed. The probable structure<sup>20</sup> of this complex for the *cis* isomer is shown below. After the complex forms, about 2 mole percent acetone



is added. The thermodynamic driving force for the transformation of the *cis* isomer to the *trans* isomer is the decrease in steric interaction between the axial and equatorial aluminate moiety. The proposed mechanism for the conversion is shown in Scheme 2. The mechanism as shown has **Scheme 2.** Conversion of *cis*-4-*t*-butylcyclohexyl alcohol to *trans*-4-*t*-butylcyclohexyl alcohol



two steps. The degree to which these two steps are concerted is not entirely clear. Within the proposed mechanism, additional acetone does not effect the *cis:trans* ratio. However, additional acetone results in an increase of 4-*t*-butylcyclohexanone recovered in the final product. The further increase in the *trans:cis* ratio was accomplished by fractional crystallization of the corresponding tosylates.

The ***trans-4-OTs*** was slowly recrystallized 4 times from petroleum ether. The recrystallization was stopped before completion each time. The ultimate recovery of product was only 0.831 g (7.4%) from an original 11.19 g. In this way, the 98:2 ratio was improved significantly. The 300 MHz NMR (Figure 1) indicates a *trans:cis* ratio of greater than 99:1. The melting point of the final product was 89.0-90.0 °C, literature<sup>19</sup> value 89.2-90.0 °C.

#### NMR of *trans-4-t*-butylcyclohexyl tosylate

The 300 MHz NMR spectrum of ***trans-4-OTs*** reveals many fine structural details that confirm the diequatorial conformation of the isomer (see Figure 1). An epimeric purity of greater than 99% is also verified. The spectrum can be separated into four spin systems. Two are in the *t*-butylcyclohexyl portion and the other two are in the toluenesulfonyl moiety.

One of the important aspects to note in the NMR spectrum is the very sharp splitting pattern. This indicates that the

spatial relationships between coupled nuclei are frozen with respect to the time frame of the experiment. The only conformation that is at all likely is the diequatorial one. If there were conformational changes from diequatorial to diaxial, the spectral lines would broaden.

The methyl resonance of the toluenesulfonyl moiety appears as a singlet at 2.44 ppm. The aromatic hydrogens appear downfield. The two protons *ortho* to the methyl group are centered at 7.33 ppm and appear as a doublet of doublets. The resonance is split by the protons *meta* to the methyl group with a coupling of 7.8 Hz. This doublet is then split by the protons across the ring with a smaller coupling constant of 0.6 Hz. The protons *meta* to the methyl group appear further downfield, due to the inductive effects of the sulfoxyl group, and are centered at 7.79 ppm. These protons are coupled with the *ortho* protons with a coupling constant of 8.4 Hz. As with the *ortho* protons, this resonance shows evidence of cross ring coupling. The precise value of the coupling constant could not be determined. The *t*-butylcyclohexyl portion of the molecule does not give a first order spectrum. However, the information that it does provide verifies an epimeric purity of greater than 99% in the *trans* configuration. The proton on the same carbon as the *t*-butyl group appears as a nonet centered at 4.34 ppm. Upon closer inspection, however, it is a triplet of triplets. The two axial protons alpha split the peak into a triplet with a coupling constant of 11.4 Hz. This triplet is then

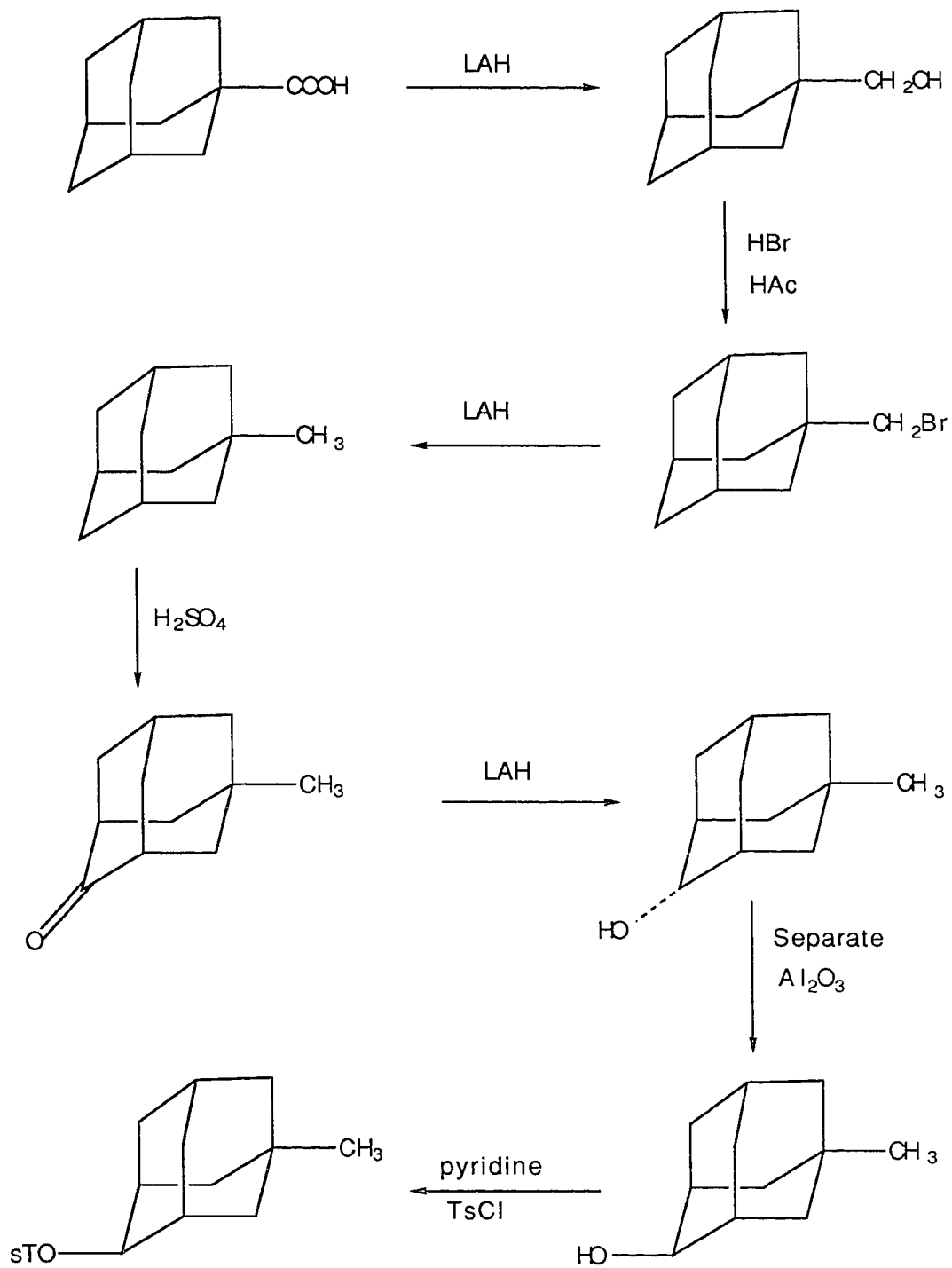


split by the two alpha equatorial protons with a much less efficient coupling of 4.8 Hz. The sharpness of these peaks indicates that the coupling protons are chemically different on the time scale of the NMR experiment. This is another clue as to the locked diequatorial conformation of the molecule. The remaining aliphatic protons are assigned as follows. H<sub>a</sub> (the protons equatorial and alpha to tosylate), 1.96 ppm; H<sub>b</sub> (the protons axial and alpha to tosylate), 1.76 ppm; H<sub>c</sub> (the protons equatorial and beta to tosylate), 1.42 ppm; H<sub>d</sub> (the protons axial and beta to tosylate), 0.97 ppm. Equatorial protons are observed further downfield due to the anisotropic deshielding effects of the circulating electrons in the C2-C3 bond and the locked conformation of the cyclohexyl ring.<sup>21</sup>

The range between 4.3 ppm and 7.1 ppm was integrated. No peak greater than 1% of the axial proton was observed. This verifies a purity of at least 99% for the ***trans*-4-OTs**.  
Attempted Synthesis of 1-Methyl-4-Adamantyl Tosylate

The complete synthesis of 1-methyl-4-adamantanol from 1-adamantane carboxylic acid was not accomplished. The procedure outlined by Whiting et al.<sup>22</sup> called for a series of selective oxidations and reductions beginning with 1-adamantane carboxylic acid (see Scheme 3). It was possible to reproduce some of his work. However, reproducible synthesis of 1-methyl-4-adamantanone was never accomplished.

Scheme 3



1-Adamantane carboxylic acid was reduced to 1-hydroxymethyladamantane in 100% yield with lithium aluminum hydride. 1-Hydroxymethyladamantane was refluxed in HBr/H<sub>2</sub>SO<sub>4</sub> to afford 1-bromomethyladamantane in 95% yield. Whiting called for HBr in acetic acid for this reaction. We found that these conditions led largely to acetate products, both by displacement and rearrangement. 1-Methyladamantane was prepared in 73% yield by reduction of the bromide with lithium aluminum hydride for 48 hrs. For the reduction of the bromide, Whiting called for an excess of **LAH** in ethyl ether. We found that these conditions resulted in a significant amount of product that was isomeric with methyladamantane by MS and NMR. Presumably this compound is the ring expansion product, tricyclo[3,3,2,1]undecane. Whether or not Whiting obtained similar results is uncertain. It is possible that Whiting did, and that the subsequent sulfuric acid oxidation rearranged the alkane *in situ* to yield substituted adamantane derivatives. Whiting does point out that many products result from the oxidation of 1-methyladamantane and that the mechanisms are not completely elucidated.

The conditions that were used to reduce the bromide were a molar excess of **LAH** in tetrahydrofuran under reflux for 3 days. It was assumed that with only an equivalent of **LAH** that the reduction proceeded to 1/4 completion. It is suspected that upon 1/4 completion a monobromoaluminate

complex is formed leading to a decrease in the rate of reduction relative to the rate of rearrangement.

The isolation of 1-methyl-4-adamantanone from the oxidation of 1-methyladamantane was not accomplished. Several reaction conditions were attempted. They included ozonolysis on silica gel, free radical chlorination, chromic acid oxidation, and careful variations of the temperature and time of reaction. The reaction conditions which gave the most promising results were 96% sulfuric acid under reflux for 8 hrs. Starting with 30 mg, we isolated 20% yield of a product with a mass spectrum that was consistent with 1-methyl-4-adamantanone (See Figure 2). However, all attempts to scale up the reaction ended in one of two results: 1) complete destruction of starting material or 2) recovery of unreacted starting material.

#### Kinetic Studies

Kinetic studies on **2-Ad-OTs** and **trans-4-OTs** were performed using a sealed ampule technique. The initial concentration of **2-Ad-OTs** was typically 2 mM, and **trans-4-OTs** was typically 5 mM. In the case of **2-Ad-OTs**, the concentration of the unreacted tosylate ester was monitored spectrophotometrically at 263 nm. The kinetic solutions were unbuffered.

For **trans-4-OTs** the concentration of the elimination product 4-*t*-butylcyclohex-1-ene was followed by GC/MS. *para*-Xylene was used as an internal standard, and 8 mM triethyl amine buffer was added to the kinetic points. The

preferred buffer, collidine, coeluted with one of the reaction products and could not be used. Close monitoring of the products showed that the ratio of reaction products remained unchanged throughout the reaction. The rate constants were calculated from the time and absorbance or concentration data using the standard LSKIN method.<sup>23</sup> Correlation coefficients were greater than 0.99 and first-order kinetics were observed in all cases. For **2-Ad-OTs**, rate constants are typically the average of three determinations. The rate constants for **trans-4-OTs** are typically single measurements. The concentration vs. time data for **trans-4-OTs** proved to be superb (see Figure 3) with typical errors in the measured LSKIN k of less than 1 percent. The measured rates as a function of solvent composition and temperature are listed in Tables III and IV for **2-Ad-OTs** and **trans-4-OTs**, respectively. The rates for **1-Ad-OTs** are listed in Table v.<sup>4</sup>

On examination of the solvolysis rates for **1-Ad-OTs**, **2-Ad-OTs**, **trans-4-OTs**, and methyl tosylate, it is observed that the rate ratio  $K_{\text{TFE}}/K_{\text{EtOH}}$  decreases from 10,000 to 1000 to 3.5 to 0.01, respectively<sup>24</sup>. This decrease in rate ratio parallels the change in the mechanism of reaction. In **1-Ad-OTs**, the backside of the reacting center is completely blocked, and solvolysis presumably proceeds via an  $S_{\text{N}}1$  reaction. The backside of the reacting center in methyl tosylate is for all purposes unhindered. This substrate

reacts via an  $S_N2$  mechanism. The direct displacement reaction is of lower energy than the reactions that proceed through a catenoid intermediate. The result is that methyl tosylate reacts faster in ethanol, relative to TFE, than does **1-Ad-OTs**.

#### Product Studies

The advent and refinement of GC/MS spectroscopy has made the once experimentally difficult task of performing product studies much less tedious. The criteria that must be met to do meaningful product studies in the mM range are: 1) high reproducibility and 2) high sensitivity. A Finnigan 1020B GC/MS/DS fulfills these needs admirably. The capillary GC successfully separates the ethyl and 2,2,2-trifluoroethyl ethers of all products of interest. This is true even in the case of the epimeric *trans-t*-butylcyclohexyl ethers. In order to gain the highest sensitivity and best reproducibility, the MS was programmed to monitor only selected ions of interest in the solvolytic products. This selected ion monitoring has three advantages over full scan monitoring.

- 1) Since the MS looks only for ions that are present in the mass spectrum, it does not waste time monitoring mass ranges that do not contain peaks of significant intensity. In this way, the sensitivity is increased by as much as 50 fold relative to full scan monitoring.

- 2) The reproducibility of the quantitation is increased by virtue of increased signal to noise ratio and the significant increase in baseline resolution.
- 3) Since the MS monitors peaks that are unique to the solvolysis products, the residual solvent is not observed. By the same reason, spurious impurities are not observed. This gain affords a very stable baseline. This is another factor that gives rise to improved reproducibility.

The reconstructed ion chromatogram (RIC) for the 5 solvolysis products of **trans-4-OTs** is shown in Figure 4. The mass spectra of the 5 major solvolysis products in respective order of their elution are shown in Figures 5-9.

#### Substrate Selectivity vs. Rate Ratio

As was noted earlier, the progression from **1-Ad-OTs** to methyl tosylate changes the character of the solvolysis reaction from  $S_N1$  to  $S_N2$ . This change is reflected in the rate ratios. Not surprisingly, the selectivity of the substrate for TFE also decreases when going from **1-Ad-OTs** to methyl tosylate. There are no products formed from the backside in **1-Ad-OTs**. Therefore, the products reflect the abundance of TFE associated with the tosylate ester in the ground state. Methyl tosylate solvolyzes to give largely products of inverted stereochemistry.<sup>25</sup> This process clearly

favors ethanol. The selectivity for **1-Ad-OTs**, **2-Ad-OTs**, and **trans-4-OTs** is presented in Figures 10-12, respectively. Based on N values the selectivity of methyl tosylate can be approximated at 0.001. The decrease in selectivity for these compounds parallels the decrease in rate ratios.

#### Product Studies for 1-Ad-OTs and 2-Ad-OTs

As mentioned previously, 2-adamantyl substrates have been used by some workers as a model for limiting  $S_N1$  behavior and for developing a Y scale, even in light of the work by Bunnett and Paradisi. Our work in investigating the kinetics and products of solvolysis of **1-Ad-OTs** and **2-Ad-OTs** indicates that there is significant product formation and rate enhancement via reaction at the back face of the reacting center. The product distributions for **2-Ad-OTs** and **1-Ad-OTs** are shown in Tables VI and VII, respectively. The results from the product studies can be conveniently discussed within the context of an excess function. An excess (XS) function for the formation of the ROTFE product is shown in equation 2:

$$\text{excess ROTFE (XS)} = X_{(\text{ROTFE})} - X_{(\text{TFE})} \quad (2)$$

Where  $X_{(\text{ROTFE})}$  is equal to the mole fraction of TFE ether products relative to ROEt and  $X_{(\text{TFE})}$  is the mole fraction of TFE relative to EtOH in the solvent medium.

The excess function provides a simple method of evaluating the observed product distributions with respect to



the solvent composition. If products are formed in the same proportions as the bulk solvent, then the excess ROTFE is zero and the substrate shows no selectivity for either solvent. The excess ROTFE vs. mole fraction TFE for **1-Ad-OTs** and **2-Ad-OTs** are shown in Figures 13 and 14. The excess plot for the difference between **1-Ad-OTs** and **2-Ad-OTs** is shown in Figure 15. If we accept that **1-Ad-OTs** is the model for frontside reaction and that **2-Ad-OTs** is a composite of frontside and backside reactions, then Figure 15 represents the excess plot for reaction at the backside. Perhaps the most evident feature in Figures 13 and 14 is that TFE ethers are in excess at all compositions. Furthermore, **1-Ad-OTs** shows a larger excess at all compositions. Similarly, reaction at the backside in **2-Ad-OTs** shows excess ethyl ether at all compositions.

Another function commonly used to evaluate data from product studies is the selectivity.<sup>26</sup> The selectivity function is defined in equation 3:

$$\text{Selectivity} = \frac{k(\text{sol-1})}{k(\text{sol-2})} = \frac{[\text{ROsol-1}][\text{sol-2}]}{[\text{ROsol-2}][\text{sol-1}]} \quad (3)$$

The product ratios vs. solvent ratios for **1-Ad-OTs**, **2-Ad-OTs** and backside **2-Ad-OTs** are shown in Figures 10, 11 and 16, respectively. In these plots, the curvature that was present in the excess plots has been eliminated, and within experimental error, the data can be expressed linearly. The slope of the line at any given point is equal to the

selectivity at that point. A linear plot indicates constant selectivity.

trans-t-Butylcyclohexyl tosylate

The product studies for **trans-4-OTs** are interesting. These results are generally consistent with the hypothesis that there are different mechanisms for frontside and backside reactions. The product distributions for solvolysis of **trans-4-OTs** are presented in Table VIII. The four ether products have been normalized and are presented in Table IX. The normalized results, when the *cis* products are normalized independently of the *trans* products, are given in Table X. Treating the data in this manner allows for comparisons between the **1-Ad-OTs/2-Ad-OTs** model and **trans-4-OTs**.

Figure 12 shows the overall selectivity for **trans-4-OTs** with respect to ether products. The overall selectivity favors EtOH. The TFE selectivity values range from 0.24 to 0.63. If evaluated as a straight line, the TFE selectivity is 0.586 with a correlation coefficient of 0.998. These values are in contrast to the constant TFE selectivity of 1.27 for **2-Ad-OTs**. The probable cause of this difference is the alternate path of reaction for **trans-4-OTs**. The elimination product is formed from an intermediate that can proceed to form either alkene or ether products. Presumably, this intermediate would preferentially form TFE ether products, relative to ethyl ether products, if no alternate mode of reaction was available. Without this mode of reaction, it is likely that the overall selectivity would favor TFE.

By separately normalizing the *cis* and *trans* products the selectivities for both backside and frontside reactions can be evaluated. It is evident that the formation of products on opposite faces is different. The product ratio vs. solvent ratio plots for *trans* and *cis* products, respectively, are shown in Figures 17 and 18. Reaction with retained configuration affords a nearly linear selectivity plot with a TFE selectivity of 4.21, and a correlation coefficient of 0.993. The data for products of inverted configuration cannot be approximated by a straight line (correlation coefficient less than 0.98). However, the values for selectivity with respect to TFE are within the range of 0.0 to 0.055.

The amount of elimination product versus mole fraction ethanol is given in Figure 19. The plot is linear (cc. 0.998) from 29.5% alkene at  $X_{\text{EtOH}} = 1$ , to 76.5% at  $X_{\text{EtOH}} = 0$ . As one progresses from  $X_{\text{EtOH}} = 0$  to  $X_{\text{EtOH}} = 1$ , the solvent becomes more nucleophilic at the expense of electrophilicity and acidity. At the more nucleophilic end of the spectrum, ethanol is able to "push" the leaving group better than TFE. This gives a tighter transition state and one that is less likely to lose a proton to afford alkene.

#### Kinetic Analysis

The rates for ***trans-4-OTs*** were measured in four different compositions of EtOH/TFE (Table IV) and have already been discussed. The log rate of solvolysis correlates linearly with the mole fraction solvent (correlation coefficient of 0.995). The data is interpolated

and extrapolated throughout the entire solvent range and is shown in Figure 20. The extrapolation of this data is justified by the demonstrated linearity observed in the log rates of other similar alkyl substrates in EtOH/TFE media. Some of the substrates that have shown linear log rate vs. composition behavior are **1-Ad-OTs**, **2-Ad-OTs**, 1-bicyclo[2,2,2]octanyl tosylate and *t*-butyl chloride.<sup>2,4</sup> As mentioned previously, it was shown that the products of solvolysis were formed in a constant ratio throughout the course of the reaction. This is expected for a reaction proceeding under irreversible conditions, where equilibration is not significant.

The rate of solvolysis is obtained by following the appearance of any of the products vs. time. The actual rate of formation of product is then the solvolysis rate multiplied by the fractional composition of that specific product. When these log rates are plotted vs. mole fraction TFE, only the curve for the alkene product is linear. See Figures 21-25. The corresponding plots for the ether products are decidedly non linear.

Recall however, that a linear solvolysis rate plot is generally interpreted as a reaction which proceeds via a constant mechanism within the composition change of interest. Yet, the linear plot (Figure 20) is a composite of five other curves, all but one of which is non linear. This discrepancy

will not be addressed at this time, rather an analysis of the individual curves will be offered.

The log rate for the alkene formation vs. mole fraction TFE is shown in Figure 21. Within experimental error this is linear (slope of 1.2). Two apparent conclusions can be drawn from this result: 1) the plot is linear, consistent with a constant mechanism for the elimination pathway; and, 2) the rate is faster in TFE than in ethanol, consistent with separation of substrate and leaving group with electrophilic solvent assistance favoring TFE.

The other four log rate vs. mole fraction TFE plots are all non linear. The shapes of the curves may offer insight into the mechanism(s) by which the specific products are formed in addition to a more general mechanism by which solvolysis reactions proceed. The log rate for the formation of the *trans* ethyl ether is shown in Figure 24. The curve is parabolic in appearance with a maximum at ca. 0.55 mole fraction TFE. The rate is enhanced by the addition of TFE into pure ethanol and by the addition of ethanol into pure TFE. This strongly suggests a bimolecular process. Presumably, TFE is providing assistance to ionization while ethanol is replacing the tosylate moiety. It seems reasonable then, that the maximum effect should be at approximately equimolar concentration of each solvent.

The log rate plot for the formation of the *cis* ethyl ether is shown in Figure 25. This product results from backside reaction of ethanol to give product of inverted

configuration. The rate increases slightly with the addition of small amounts of TFE to ethanol. The rate remains roughly constant to about 0.4 mole fraction TFE even though the amount of ethanol (the solvent which is incorporated into the product) is decreasing. This is not the expected result for a first-order reaction. A reasonable mechanism could be proposed which involves an electrophilic pull by TFE concomitant with a nucleophilic push on the leaving group by ethanol.

The log rate for the formation of the *cis*-TFE ether is shown in Figure 22. This product is the result of reaction of TFE to give products of inverted configuration. This reaction is slower than all other reactions by at least one order of magnitude, and shows the greatest change in rate over the entire composition range. This 100 fold change in rate is a manifestation of TFE assisting on both frontside and backside. Both influences increase with increasing TFE concentration. This can be contrasted with the other ether-producing reactions that are dependent on both solvents. The solvents are complimentary and necessarily one solvent concentration is increasing while the other is decreasing.

The log rate plot for the formation of the *trans*-TFE ether is shown in Figure 23. The change in rate for this reaction is nearly as large as for the reaction forming the *cis*-TFE ether. Presumably, the reasons are similar.

Though the precise mechanism of reaction may never be known, the rate data for the individual products provides

strong support for a delineation between frontside and backside reactions. Ethanol, the better nucleophile, prefers to actively displace the leaving group and TFE prefers to assist in bond cleavage and form products of retained configuration.

These data are firm evidence that interpretations of linear rate vs. composition plots should be approached with some trepidation. It would seem preferable if general conclusions were not offered for linear rate plots. Instead, specific reactions should warrant specific interpretations.

#### Alkene stability test

To insure that the results of solvolysis were the kinetic products and not the thermodynamic products, buffered methylcyclohexene was allowed to react with TFE under the reaction conditions at 120 °C for four days. The mixture was analyzed and no trace of ether products were observed. Similar work has shown that transesterification is statistically insignificant after 1000 half lives.<sup>4</sup>

#### 1-Bicyclo[2,2,1]carbinyl Tosylate Products

The results from **trans-4-OTs** are consistent with the observed products of solvolysis of 1-bicyclo[2,2,1]heptan carbinyl tosylate in various solvents. The results of this study are given in Tables **XI**, **XII** and **XIII**. The lack of hydrogen alpha to the tosylate carbon in this molecule precludes 1,2-elimination. The observed products must then be the result of direct displacement on the carbinyl carbon,

or bond migration to form either 1-bicyclo[3,2,1]octanyl or 1-bicyclo[2,2,2]octanyl products. The intermediate from which the 1-bicyclo-octanyl products are formed is analogous to the *trans*-*t*-butyl intermediates, which affords elimination products. The results of solvolysis show that bond migration is much more likely in TFE than in ethanol, just as elimination is more likely in ***trans*-4-OTs**.

The results for solvolysis of 1-bicyclo[2,2,1]heptan carbinyl tosylate in ethanol as a function of temperature are given in Table **XII**. These data are plotted and shown in Figure 26. It can be seen that as the temperature decreases, the relative amount of unrearranged product increases. The mechanism that produces carbinyl products certainly maintains a great deal of S<sub>N</sub>2 character. The bond migration to form rearranged products must proceed through some catenoid intermediate. The separation of charge in this case makes it the higher energy process. It would appear that the transition state for this reaction involves ethanol strongly coordinated at the backside of the departing tosylate moiety.

The results from the solvolysis in TFE show a very different behavior. At 90 °C only 1.3% of the product has not undergone skeletal rearrangement (Table **XI**). The other 98.7% has rearranged, to give either 1-bicyclo[2,2,2]octanyl TFE ether or 1-bicyclo[3,2,1]octanyl TFE ether. These two products presumably are formed via a common intermediate. It appears that in this case the preferred mechanism favors an



intermediate with more cationic character. The difference in products must somehow be a function of the solvent. As mentioned earlier, the main differences between ethanol and TFE are their pKa's and nucleophilicity. Both of these differences explain the product distributions. TFE is more acidic and therefore associates via hydrogen bonding better to tosylate than ethanol. Since TFE is less nucleophilic than ethanol, it does not afford the same degree of nucleophilic stabilization and therefore the reaction proceeds through a catenoid intermediate.

Both of these factors give rise to a looser transition state with a higher degree of positive charge developed on carbon. Since elimination is not a possibility for 1-bicyclo[2,2,1]heptan carbinyl tosylate, the corresponding products show more rearrangement. This trend, where higher acidities combined with lower nucleophilicities give rise to more rearrangements, is evident in the results listed in Table **XI**. For the following solvents, trifluoroacetic acid (TFA), acetic acid (AcOH), TFE, EtOH, and isopropanol (IPA), the acidity decreases and the nucleophilicity increases in the order given. The amount of product encompasses the entire spectrum, from 100% rearrangement in TFA to 0% rearrangement in IPA.

These data are consistent with most interpretations of reactions of neopentyl systems. The reacting carbon in 1-bicyclo[2,2,1]heptan carbinyl tosylate is primary and needs nucleophilic assistance for reaction to proceed. In those

solvents that are nucleophilic the products favor direct displacement, presumably through and  $S_N2$ -like reaction. In those solvents that are nonnucleophilic, the substrate must seek internal nucleophilic stabilization, and hence the products are of a rearranged configuration.

### Conclusion

The nature of the solvents are at least as important as the substrate in determining the products and kinetics for a solvolysis reaction. The lifetime of any reaction intermediate for simple alkyl tosylates is short. Therefore the reaction intermediate must select from the available micro solvent pool to afford products, i.e. the existence of a solvent separated ion pair seems unlikely for these systems. This micro solvent pool is determined by many factors, some of which are, substrate and leaving group size, hydrogen bonding capability of the leaving group/substrate, solvent acidity, and solvent electrophilicity. If the rate determining step is not bond cleavage to give an internal ion pair and if **2-Ad-OTs** and **trans-4-OTs** solvolyze with significant reaction from the backside then two things are evident: 1) **2-Ad-OTs** is not a suitable model compound for  $S_N1$  reactions and 2) the value of  $\rho$  is a composite of multiple solvent parameters thus making the  $\rho$  treatment of solvolysis data of little value for mechanistic interpretations.

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## Experimental

Melting points were obtained on a Fischer-Johns melting point apparatus and are uncorrected. Infrared spectra were obtained as solution in chloroform or carbon tetrachloride on a Perkin Elmer IR-257 spectrophotometer. Gas chromatographic and mass spectral analyses were performed on a Finnigan 1020B GC/MS/DS fitted with a 30 meter DB5 silicone oil column. A Beckman 25 UV-VIS was used for spectrophotometric measurements. NMR analysis was performed with a Bruker 300 MHz NMR.

**Solvents.** Trifluoroethanol was obtained from Aldrich and was dried by reflux with a soxhlet extractor packed with dried 4 angstrom molecular sieves for a minimum of 24 hours. Ethanol was distilled from powdered 4 angstrom sieves immediately prior to use.

**1-Adamantane carboxylic acid** was purchased from Lancaster synthesis and was found to be greater than 99% pure by gas chromatography.

**1-Hydroxymethyl adamantane.** 1-Adamantane carboxylic acid (96.70 g, 0.537 Mol) was dissolved in ca. 500 mL ethyl ether, lithium aluminum hydride (28 g, 0.74 Mol) in 200 mL ethyl ether was added dropwise over 2 hours. This reaction mixture was allowed to stand 24 hours. The solution was then acidified with HCl (6M). The aqueous layer was extracted with ethyl ether. The ether extracts were combined and dried over  $MgSO_4$ . The ether was removed in vacuo to afford 89.2 g

(100%) of the desired product. m.p. 117-117.5 °C. IR (CCl<sub>4</sub>) 3625 (strong) C-OH, loss of 2900 to 3400cm<sup>-1</sup>.

**1-Bromomethyl adamantane.** 1-hydroxymethyl adamantane (8.434 g, 36.8 mMol) was combined with 30 mL hydrobromic acid (48%) and then 10 mL sulfuric acid (98%). The inhomogeneous reaction mixture was refluxed for 6 hours. The mixture was extracted with ethyl ether (3x75 mL). The ether was washed with 5% NaHCO<sub>3</sub> until no CO<sub>2</sub> evolved, and then with saturated NaCl. The ether was dried over MgSO<sub>4</sub>, filtered and the ether was removed under reduced pressure to afford 11.00 g (95%) light brown powder m.p. 42.5-43 °C, lit<sup>7</sup> m.p. 42.5-43 °C. IR (CCl<sub>4</sub>) 2920-2980(s) C-H, 2650-2700 (med), loss of 3625cm<sup>-1</sup>. NMR (CCl<sub>4</sub>), delta 3.05 (singlet) 2-H's.

**1-Methyl adamantane.** To a solution of lithium aluminum hydride (10 g, 0.25 Mol) in tetrahydrofuran (200 mL), 50.38 g 1-adamantylmethyl bromide in tetrahydrofuran was added over 1 hour. The solution was refluxed for 72 hours. The excess lithium aluminum hydride was decomposed with wet tetrahydrofuran. The majority of the tetrahydrofuran was removed *in vacuo*. Caution was taken to avoid the sublimation of the alkane. The residue was extracted with ethyl ether. The ether was washed with 5% NaHCO<sub>3</sub>, and saturated NaCl. The ether was removed under reduced pressure without the aid of external heat. A waxy white oily solid (23.4 g, 71%) was

recovered. (90% pure GC/MS analysis), the remaining 10% was an isomer, presumably tricyclo[3,3,2,1]undecane.

**1-Methyl-4-adamantanone.** 1-methyladamantane (41 mg, 0.27 mMol) and sulfuric acid (2 mL, 97%) were combined in a 2 mL ampule. The ampule was placed in a constant temperature bath at 75 °C for 18 hours. After 6 hours undissolved materials were observed. After 18 hours the reaction mixture was dark brown and no indication of undissolved materials remained. The reaction mixture was partially neutralized with 5 mL 5% NaHCO<sub>3</sub>. The mixture was extracted with 25 mL ethyl ether. The ether was washed with 5% NaHCO<sub>3</sub> (25 mL), and saturated NaCl (25 mL). The ether was dried over MgSO<sub>4</sub> and removed *in vacuo* to afford a clear oil (23 mg, 51%). Of the 23 mg, 40% (GC) affords a mass spectrum that is consistent with the desired product. See Figure 2.

**2-Adamantyl tosylate.** 2-Ad-OTs was prepared from 2-adamantanol and toluenesulfonyl chloride in pyridine. The crude solid was recrystallized from petroleum ether.

***trans*-4-*t*-Butylcyclohexyl alcohol (92.5%).** 4-*t*-butylcyclohexyl alcohol (14.04 g, 0.090 Mol), (25% *cis*:75% *trans*) was dissolved in 100 mL ethyl ether. This solution was slowly added to a mixture of anhydrous aluminum chloride (13.37 g, 0.1000 Mol) and lithium aluminum hydride (1.4 g, 0.037 Mol). The solution was refluxed for 2 hours, after which acetone (2.61 g, 0.045 mol) was added. The solution turned yellow and was refluxed for an additional one

hour. Twenty milliliters water and 300 mL sulfuric acid (3M) was added and the mixture was allowed to stand overnight. The reaction mixture was extracted with ethyl ether. The ether was washed with 5% NaHCO<sub>3</sub> (2x50 mL), saturated NaCl (2x50 mL) and dried with MgSO<sub>4</sub>. The solution was filtered and the ether was removed under reduced pressure to afford 12.15 g (86%) yellow solid with a *trans*:*cis* ratio of 92.5:7.5 (GC). Recrystallization from pet ether did not improve this ratio.

***trans*-*t*-Butylcyclohexyl alcohol (95.5%).**

4-*t*-butylcyclohexyl alcohol (12.15 g, 0.0779 Mol), (92.5% *trans*:7.5% *cis*) was dissolved in ether and added to a solution of anhydrous aluminum chloride (10.37 g, 0.0779 Mol) and lithium aluminum hydride (0.88 g, 0.0232 Mol). The solution was refluxed for 2 hours and kept at ambient temperature overnight. Acetone (5.4 mL, 0.0735 Mol) was added and the solution turned deep red in color. After 10 minutes 200 mL sulfuric acid (3M) was added and the reaction was worked up as before. Analysis of the 11.57 g white solid indicated a 95.5:4.5 *trans*:*cis* ratio.

***trans*-4-*t*-Butylcyclohexyl alcohol (98.0%).**

4-*t*-butylcyclohexyl alcohol (11.57 g, 0.0742 Mol), (95.5%*trans*:4.5%*cis*) was dissolved in ether and added to a solution of anhydrous aluminum chloride (9.86 g, 0.0740 Mol) and lithium aluminum hydride (0.83 g, 0.0219 Mol). The reaction was worked up as before to yield 11.19 g white solid, 98% *trans* by GC.

**trans-4-t-Butylcyclohexyl tosylate** was prepared by the standard pyridine method from the alcohol and toluene sulfonyl chloride. The white solid product was recrystallized slowly from petroleum ether 4 times. The crystallization was stopped at about 1/2 completion each time. The final yield was 0.831 g with a 99% epimeric purity (NMR, 300MHz).

**Kinetic points** were prepared by dissolving the appropriate amount of substrate, 2 mMolar for **2-Ad-OTs** and 5mMolar for **trans-4-OTs** in the proper amount of ethanol followed by addition of the supplemental amount of TFE. For **trans-4-OTs** triethylamine and *para*-xylene were added in 50% excess relative to **trans-4-OTs**. A sealed ampule technique was employed to obtain the kinetic samples. The concentration of **2-Ad-OTs** was monitored spectrophotometrically at 263 nm with distilled water as a reference. The concentration of 4-t-butylcyclohexene was followed by GC/MS and expressed as a percentage of *para*-xylene.

**Product Studies.** The experimental samples were prepared by dissolving *trans-4-t-butylcyclohexyl tosylate* in ethanol to give a 0.05 Molar solution. Triethyl amine and *para*-xylene were then added in 50% molar excess. An (100  $\mu$ l) aliquot of this solution was transferred to 1 mL ampules, a 2 mL ampule was used for the 5% ethanol sample. The appropriate amount of ethanol and TFE were then added to prepare solutions of approximately 100, 95, 90, 80, 70, 60, 50, 40, 30, 20, 10, and 5% ethanol by volume. The amount of ethanol



and TFE were weighed to the nearest 0.1 mg to afford the precise solvent composition. The 100% TFE samples were prepared separately at nearly the same concentration as all other samples. The samples were solvolyzed at 70 °C for 45 days. The samples were analyzed by GC/MS using the following conditions:

|                    |        |
|--------------------|--------|
| Zone Temp          | 225 °C |
| Initial Temp       | 166 °C |
| Final Temp         | 166 °C |
| Sep. Set Pt.       | 225 °C |
| Manif. Set. Pt.    | 80 °C  |
| Split/Sweep time   | 1 sec  |
| Fil/Mult. off time | 90 sec |

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**Table III.** Rate Constants for 2-Ad-OTs in Mixtures of EtOH and TFE

| %TFE<br>(v/v) | Temp <sup>a</sup><br>°C | rate 1/s<br>10 <sup>4</sup> k | $\Delta H^\ddagger$<br>Kcal/mol | $\Delta S^\ddagger$<br>(eu) |
|---------------|-------------------------|-------------------------------|---------------------------------|-----------------------------|
| 100           | 90                      | 19.7 ± 0.7                    |                                 |                             |
| 100           | 80                      | 9.20 ± 0.18                   |                                 |                             |
| 100           | 70                      | 3.52 ± 0.07                   |                                 |                             |
| 100           | 60                      | 1.18 ± 0.01                   |                                 |                             |
| 100           | 25 <sup>b</sup>         | 0.0212                        | 22.4 ± 0.4                      | -10.1 ± 1.2                 |
| 80            | 90                      | 4.41 ± 0.11                   |                                 |                             |
| 80            | 80                      | 1.63 ± 0.06                   |                                 |                             |
| 80            | 70                      | 0.656 ± 0.009                 |                                 |                             |
| 80            | 60                      | 0.225 ± 0.005                 |                                 |                             |
| 80            | 25 <sup>b</sup>         | 0.00341                       | 23.0 ± 0.5                      | -11.1 ± 1.4                 |
| 50            | 110                     | 3.78 ± 0.02                   |                                 |                             |
| 50            | 100                     | 1.45 ± 0.09                   |                                 |                             |
| 50            | 90                      | 0.555 ± 0.032                 |                                 |                             |
| 50            | 80                      | 0.200 ± 0.011                 |                                 |                             |
| 50            | 25 <sup>b</sup>         | 0.000198                      | 25.6 ± 0.8                      | -8.0 ± 2.2                  |
| 20            | 135                     | 7.74 ± 0.6                    |                                 |                             |
| 20            | 130                     | 4.62 ± 0.07                   |                                 |                             |
| 20            | 120                     | 2.03 ± 0.05                   |                                 |                             |
| 20            | 110                     | 0.808 ± 0.024                 |                                 |                             |
| 20            | 100                     | 0.305 ± 0.009                 |                                 |                             |
| 20            | 25 <sup>b</sup>         | 0.0000259                     | 26.8 ± 0.4                      | -7.7 ± 1.0                  |

<sup>a</sup>Temperature ± 0.05 °C. <sup>b</sup>Data at 25 °C extrapolated from data at other temperatures.

**Table IV.** Rate Constants for *trans*-4-*t*-Butylcyclohexyl Tosylate in Mixtures of EtOH and TFE

| %TFE<br>(v/v) | Temp <sup>a</sup><br>°C | Rate 1/s<br>10 <sup>4</sup> k | ΔH <sup>‡</sup><br>Kcal/mol | ΔS <sup>‡</sup><br>(eu) |
|---------------|-------------------------|-------------------------------|-----------------------------|-------------------------|
| 80            | 100                     | 12.0 ± 0.026                  |                             |                         |
| 80            | 90                      | 4.10 ± 0.011                  |                             |                         |
| 80            | 80                      | 1.83 ± 0.009                  |                             |                         |
| 80            | 25 <sup>b</sup>         | 0.00276                       | 23.9 ± 0.4                  | -8.48 ± 0.10            |
| 50            | 100                     | 5.77 ± 0.06                   |                             |                         |
| 50            | 90                      | 2.02 ± 0.01                   |                             |                         |
| 50            | 80                      | 0.968 ± 0.004                 |                             |                         |
| 50            | 70                      | 0.387 ± 0.001                 |                             |                         |
| 50            | 25 <sup>b</sup>         | 0.00224                       | 21.9 ± 0.9                  | -15.2 ± 0.2             |
| 20            | 120                     | 15 ± 1                        |                             |                         |
| 20            | 110                     | 7.54 ± 0.02                   |                             |                         |
| 20            | 100                     | 3.84 ± 0.02                   |                             |                         |
| 20            | 90                      | 1.50 ± 0.01                   |                             |                         |
| 20            | 80                      | 0.588 ± 0.007                 |                             |                         |
| 20            | 25 <sup>b</sup>         | 0.00141                       | 21.6 ± 1.1                  | -16.9 ± 0.2             |
| 0             | 110                     | 5.70 ± 0.009                  |                             |                         |
| 0             | 100                     | 2.47 ± 0.006                  |                             |                         |
| 0             | 90                      | 1.14 ± 0.002                  |                             |                         |
| 0             | 80 <sup>b</sup>         | 0.425                         |                             |                         |
| 0             | 25 <sup>b</sup>         | 0.00145                       | 22.3 ± 0.4                  | -15.7 ± 0.02            |

<sup>a</sup>Temperatures ± 0.05 °C. <sup>b</sup>Rates with no error limits are extrapolated from data at other temperatures.

**Table V.** Rate Constants for 1-Ad-OTs in Mixtures of EtOH and TFE at 25.4 °C

| % TFE<br>(v/v) | N(1) <sup>a</sup> | Rate 1/s<br>10 <sup>4</sup> k |
|----------------|-------------------|-------------------------------|
| 80             | 5                 | 799 ± 37                      |
| 70             | 3                 | 301 ± 8                       |
| 60             | 3                 | 108.3 ± 1.3                   |
| 50             | 3                 | 41.05 ± 0.41                  |
| 40             | 3                 | 15.62 ± 0.10                  |
| 30             | 2                 | 6.20 ± 0.06                   |
| 0 <sup>b</sup> |                   | 0.440                         |

<sup>a</sup>The number of determinations of the rate at the given solvent composition. <sup>b</sup>Extrapolated from other solvent compositions.

**Table VI.** Product Distributions for 2-Ad-OTs in EtOH/TFE at 90 °C

| %TFE<br>(v/v) | %TFE<br>mol basis | Obs % <sup>a</sup><br>2-Ad-OTFE | %XS 2-Ad-OTFE <sup>b</sup> |
|---------------|-------------------|---------------------------------|----------------------------|
| 10            | 0.0826            | 8.90 ± 0.4                      | 7.7 ± 4.9                  |
| 20            | 0.1684            | 19.41 ± 0.02                    | 15.3 ± 0.10                |
| 30            | 0.2577            | 30.77 ± 0.4                     | 19.4 ± 1.6                 |
| 40            | 0.3506            | 41.56 ± 0.57                    | 18.5 ± 1.7                 |
| 50            | 0.4475            | 52.79 ± 1.6                     | 18.0 ± 3.5                 |
| 60            | 0.5485            | 63.40 ± 0.42                    | 15.6 ± 0.8                 |
| 70            | 0.6539            | 74.30 ± 0.42                    | 13.6 ± 0.7                 |
| 80            | 0.7641            | 83.23 ± 1.1                     | 8.9 ± 1.5                  |
| 90            | 0.8794            | 90.02 ± 0.4                     | 2.4 ± 0.46                 |

<sup>a</sup>Percent 2-adamantyl TFE ether. <sup>b</sup>See page 20 for definition of %XS.



**Table VII.** Product Distributions for 1-Ad-OTs in EtOH/TFE at 90 °C

| %TFE<br>(v/v) | %TFE<br>mol basis | Obs <sup>a</sup><br>1-Ad-OTFE | %XS 1-Ad-OTFE <sup>b</sup> |
|---------------|-------------------|-------------------------------|----------------------------|
| 10            | 0.0826            | 11.94 ± 0.22                  | 44.6 ± 2.6                 |
| 20            | 0.1684            | 24.37 ± 0.29                  | 44.7 ± 1.7                 |
| 30            | 0.2577            | 36.70 ± 0.18                  | 42.4 ± 0.7                 |
| 40            | 0.3506            | 48.27 ± 0.40                  | 37.7 ± 1.1                 |
| 50            | 0.4475            | 58.34 ± 0.54                  | 30.4 ± 1.3                 |
| 60            | 0.5485            | 68.68 ± 0.40                  | 25.2 ± 0.7                 |
| 70            | 0.6539            | 77.80 ± 0.04                  | 19.0 ± 0.1                 |
| 80            | 0.7641            | 86.01 ± 0.21                  | 12.6 ± 0.3                 |
| 90            | 0.8794            | 92.90 ± 0.04                  | 5.6 ± 0.1                  |

<sup>a</sup>Percent 1-adamantyl TFE ether. <sup>b</sup>See page 20 for definition of %XS.

**Table VIII.** Product Distributions for *trans*-4-*t*-Butylcyclohexyl Tosylate in EtOH at 70 °C

| %TFE<br>(v/v) | %TFE<br>mol basis | Alkene <sup>a</sup> | C-OTFE <sup>b</sup> | T-OTFE <sup>c</sup> | C-OEt <sup>d</sup> | T-OEt <sup>e</sup> |
|---------------|-------------------|---------------------|---------------------|---------------------|--------------------|--------------------|
| 0             | 0.0000            | 29.77               | 0                   | 0                   | 68.50              | 1.54               |
| 5             | 0.0390            | 30.99               | 0                   | 0.78                | 66.75              | 1.54               |
| 10            | 0.0826            | 32.15               | 0                   | 1.48                | 65.14              | 1.61               |
| 20            | 0.1684            | 35.15               | 0.04                | 3.31                | 60.12              | 1.85               |
| 30            | 0.2577            | 39.75               | 0.10                | 5.87                | 52.34              | 1.95               |
| 40            | 0.3506            | 43.90               | 0.21                | 9.11                | 44.53              | 2.24               |
| 50            | 0.4475            | 48.92               | 0.36                | 12.69               | 35.53              | 2.32               |
| 60            | 0.5485            | 54.16               | 0.56                | 16.27               | 26.75              | 2.28               |
| 70            | 0.6539            | 60.30               | 0.87                | 18.74               | 18.3               | 1.78               |
| 80            | 0.7641            | 67.03               | 1.26                | 19.89               | 10.50              | 1.32               |
| 90            | 0.8794            | 70.79               | 1.70                | 22.31               | 4.64               | 0.57               |
| 95            | 0.9400            | 72.50               | 2.09                | 22.66               | 2.42               | 0.35               |
| 100           | 1.0000            | 76.55               | 2.14                | 21.31               | 0                  | 0                  |

<sup>a</sup>Combined percent 4-*t*-butylcyclohex-2-ene and 4-*t*-butylcyclohex-3-ene. <sup>b</sup>Percent *cis*-4-*t*-butylcyclohexyl TFE ether. <sup>c</sup>Percent *trans*-4-*t*-butylcyclohexyl TFE ether. <sup>d</sup>Percent *cis*-4-*t*-butylcyclohexyl ethyl ether. <sup>e</sup>Percent *trans*-4-*t*-butylcyclohexyl ethyl ether.

**Table IX.** Products for Solvolysis of *trans*-4-*t*-Butylcyclohexyl Tosylate, Ether products Normalized<sup>a</sup>

| %TFE<br>(v/v) | %TFE<br>mol basis | C-OTFE <sup>b</sup> | T-OTFE <sup>c</sup> | C-OEt <sup>d</sup> | T-OEt <sup>e</sup> |
|---------------|-------------------|---------------------|---------------------|--------------------|--------------------|
| 0             | 0.0000            | 0                   | 0                   | 97.80              | 2.20               |
| 5             | 0.0390            | 0                   | 1.13                | 96.64              | 2.23               |
| 10            | 0.0821            | 0                   | 2.16                | 95.48              | 2.36               |
| 20            | 0.1684            | 0.05                | 5.06                | 92.0               | 2.82               |
| 30            | 0.2577            | 0.16                | 9.74                | 86.87              | 3.24               |
| 40            | 0.3506            | 0.33                | 16.15               | 79.50              | 4.02               |
| 50            | 0.4475            | 0.70                | 24.94               | 69.81              | 4.56               |
| 60            | 0.5485            | 1.22                | 35.47               | 58.34              | 4.97               |
| 70            | 0.6539            | 2.19                | 47.21               | 46.12              | 4.48               |
| 80            | 0.7641            | 3.80                | 60.33               | 31.87              | 4.00               |
| 90            | 0.8794            | 5.84                | 76.3                | 15.87              | 1.95               |
| 95            | 0.9400            | 7.58                | 82.37               | 8.78               | 1.27               |
| 100           | 1.0000            | 9.12                | 90.88               | 0                  | 0                  |

<sup>a</sup>The values in this table were derived by normalizing all of the ether products without consideration to the alkene product. i.e. the sum of all ether products is 100%.

<sup>b</sup>Percent *cis*-4-*t*-butylcyclohexyl TFE ether. <sup>c</sup>Percent *trans*-4-*t*-butylcyclohexyl TFE ether. <sup>d</sup>Percent *cis*-4-*t*-butylcyclohexyl ethyl ether. <sup>e</sup>Percent *trans*-4-*t*-butylcyclohexyl ethyl ether.

**Table X.** Products for Solvolysis of *trans*-4-*t*-Butyl-cyclohexyl Tosylate, cis Ethers and trans Ethers Normalized<sup>a</sup>

| %TFE<br>(v/v) | %TFE<br>mol basis | cis-TFE <sup>b</sup> | trans-TFE <sup>c</sup> | cis-EtOH <sup>d</sup> | trans-EtOH <sup>e</sup> |
|---------------|-------------------|----------------------|------------------------|-----------------------|-------------------------|
| 0             | 0.0000            | 0.0                  | 0.0                    | 100                   | 100                     |
| 5             | 0.0390            | 0.00                 | 33.62                  | 100.00                | 66.38                   |
| 10            | 0.0826            | 0.00                 | 47.81                  | 100.00                | 52.19                   |
| 20            | 0.1684            | 0.05                 | 64.11                  | 99.94                 | 35.89                   |
| 30            | 0.2577            | 0.18                 | 75.05                  | 99.82                 | 24.95                   |
| 40            | 0.3506            | 0.41                 | 80.09                  | 99.58                 | 19.91                   |
| 50            | 0.4475            | 0.99                 | 84.54                  | 99.01                 | 15.46                   |
| 60            | 0.5485            | 2.0                  | 87.71                  | 97.95                 | 12.29                   |
| 70            | 0.6539            | 4.54                 | 91.33                  | 95.46                 | 8.67                    |
| 80            | 0.7641            | 10.67                | 93.78                  | 89.33                 | 6.22                    |
| 90            | 0.8794            | 26.89                | 97.51                  | 73.11                 | 2.49                    |
| 95            | 0.9400            | 46.33                | 98.48                  | 53.67                 | 1.52                    |
| 100           | 1.0000            | 100.00               | 100.00                 | 0.00                  | 0.00                    |

<sup>a</sup>The values in this table were derived by normalizing the cis ethers independently of the trans ethers. i.e. the cis ethyl ether and the cis trifluoroethyl ether sum to 100%. <sup>b</sup>Percent *cis*-4-*t*-butylcyclohexyl TFE ether. <sup>c</sup>Percent *trans*-4-*t*-butylcyclohexyl TFE ether. <sup>d</sup>Percent *cis*-4-*t*-butylcyclohexyl ethyl ether. <sup>e</sup>Percent *trans*-4-*t*-butylcyclohexyl ethyl ether. Similarly for the trans ethers.

**Table XI.** Products for Solvolysis of 1-Bicyclo[2,2,1]-carbiny1 Tosylate in Various Solvents

| Solvent <sup>a</sup> | Temp °C <sup>b</sup> | %[2,2,1] <sup>c</sup> | %[2,2,2] <sup>d</sup> | %[3,2,1] <sup>e</sup> |
|----------------------|----------------------|-----------------------|-----------------------|-----------------------|
| TFE                  | 100                  | 1.3                   | 81.6                  | 17.1                  |
| EtOH                 | 100                  | 63.1                  | 30.1                  | 6.8                   |
| AcOH                 | 130                  | n.d. <sup>f</sup>     | 81.2                  | 18.8                  |
| IPA                  | 130                  | 58.5                  | 33.3                  | 8.24                  |
| IPA                  | 90                   | 74.1                  | 24.3                  | 1.67                  |
| IPA                  | 50                   | 100.00                | n.d. <sup>f</sup>     | n.d. <sup>f</sup>     |
| TFA                  | 130                  | n.d. <sup>f</sup>     | 75.1                  | 24.9                  |
| TFA                  | 90                   | n.d. <sup>f</sup>     | 79.4                  | 20.6                  |
| TFE                  | 50                   | n.d. <sup>f</sup>     | 87.2                  | 12.8                  |

<sup>a</sup>Acidity TFA>AcOH>>TFE>EtOH≈IPA. <sup>b</sup>Temperature ± 0.05 °C. <sup>c</sup>Percent 1-bicyclo[2,2,1]carbiny1 ether or ester. <sup>d</sup>Percent 1-bicyclo[2,2,2]octany1 ether or ester. <sup>e</sup>Percent 1-bicyclo[3,2,1]octany1 ether or ester. <sup>f</sup>n.d. = not detected.

**Table XII.** Products of Solvolysis of 1-Bicyclo[2,2,1]-carbinyl Tosylate in EtOH as a Function of Temperature

| Temp <sup>o</sup> C <sup>a</sup> | %[2,2,1] <sup>b</sup> | %[2,2,2] <sup>c</sup> | %[3,2,1] <sup>d</sup> |
|----------------------------------|-----------------------|-----------------------|-----------------------|
| 130                              | 46.9                  | 42.3                  | 10.8                  |
| 120                              | 54.2                  | 36.9                  | 8.93                  |
| 110                              | 58.3                  | 33.8                  | 7.92                  |
| 100                              | 63.1                  | 30.1                  | 6.81                  |
| 90                               | 69.1                  | 25.                   | 5.30                  |
| 50                               | 90.5                  | 9.5                   | 0                     |

<sup>a</sup>Temperature  $\pm$  0.05<sup>o</sup>C. <sup>b</sup>Percent 1-bicyclo[2,2,1]carbinyl ethyl ether. <sup>c</sup>Percent 1-bicyclo[2,2,2]octanyl ethyl ether. <sup>d</sup>Percent 1-bicyclo[3,2,1]octanyl ethyl ether.

**Table XIII.** Products of Solvolysis of 1-Bicyclo[2,2,1]-carbinyl Tosylate in EtOH:TFE (50:50) v/v

| temp <sup>a</sup><br>°C | %[2,2,1] <sup>b</sup><br>OEt | %[2,2,2] <sup>c</sup><br>OEt | %[3,2,1] <sup>d</sup><br>OEt | %[2,2,2] <sup>e</sup><br>TFE | %[3,2,1] <sup>f</sup><br>TFE |
|-------------------------|------------------------------|------------------------------|------------------------------|------------------------------|------------------------------|
| 130                     | 10.70                        | 7.64                         | 28.50                        | 11.37                        | 41.86                        |
| 90                      | 11.26                        | 5.54                         | 27.13                        | 9.35                         | 46.71                        |
| 50                      | 19.54                        | 3.55                         | 27.00                        | 3.55                         | 46.37                        |

<sup>a</sup>Temperature  $\pm$  0.05 °C. <sup>b</sup>Percent 1-bicyclo[2,2,1]carbinyl ethyl ether. <sup>c</sup>Percent 1-bicyclo[2,2,2]octanyl ethyl ether. <sup>d</sup>Percent 1-bicyclo[3,2,1]octanyl ethyl ether. <sup>e</sup>Percent 1-bicyclo[2,2,2]octanyl TFE ether. <sup>f</sup>Percent 1-bicyclo[3,2,1]octanyl TFE ether.

Figure 1: 300MHz NMR of *trans*-4-*t*-butylcyclohexyl tosylate

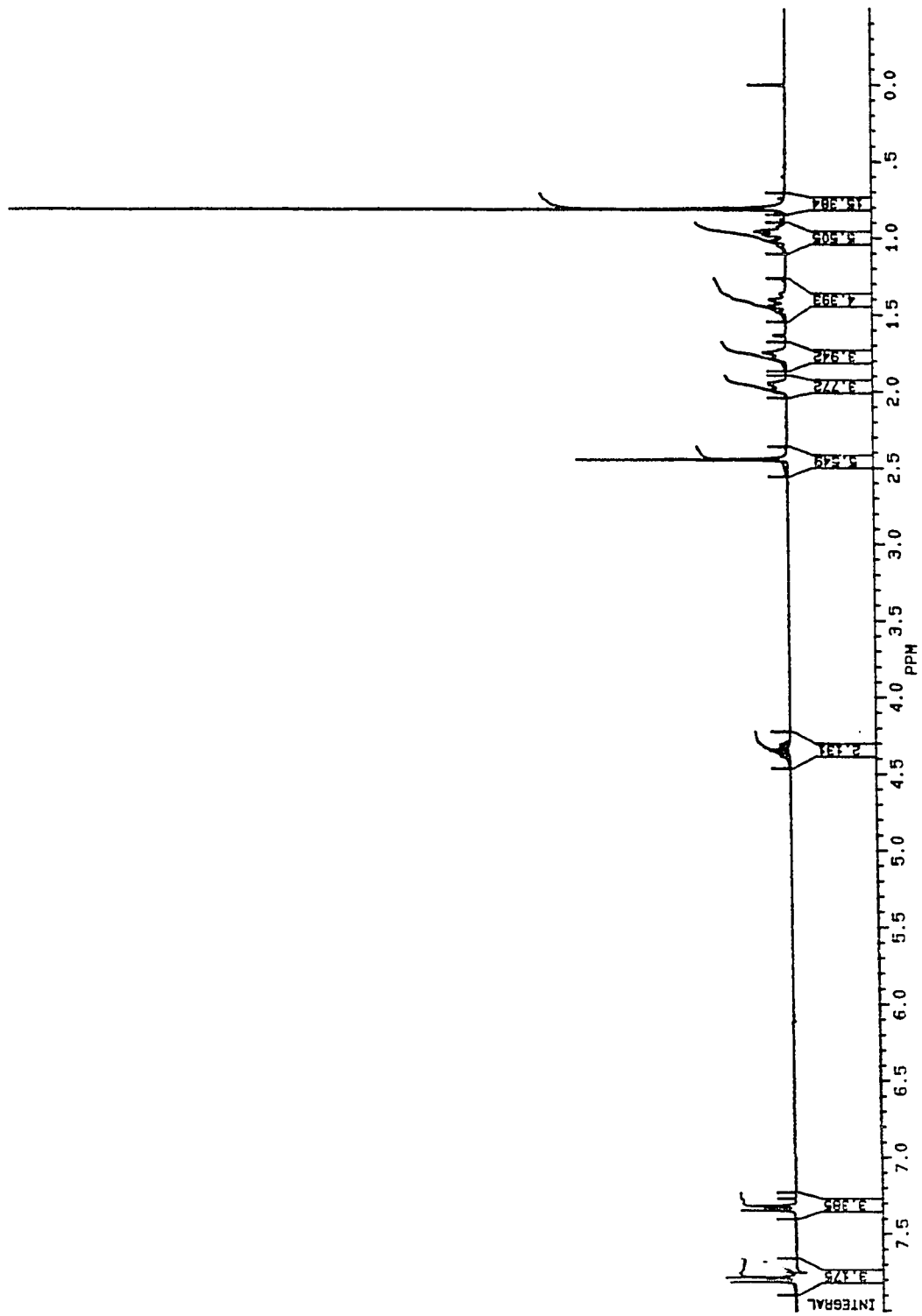




Figure 2: Mass spectrum of product from sulfuric acid oxidation of 1-methyladamantane

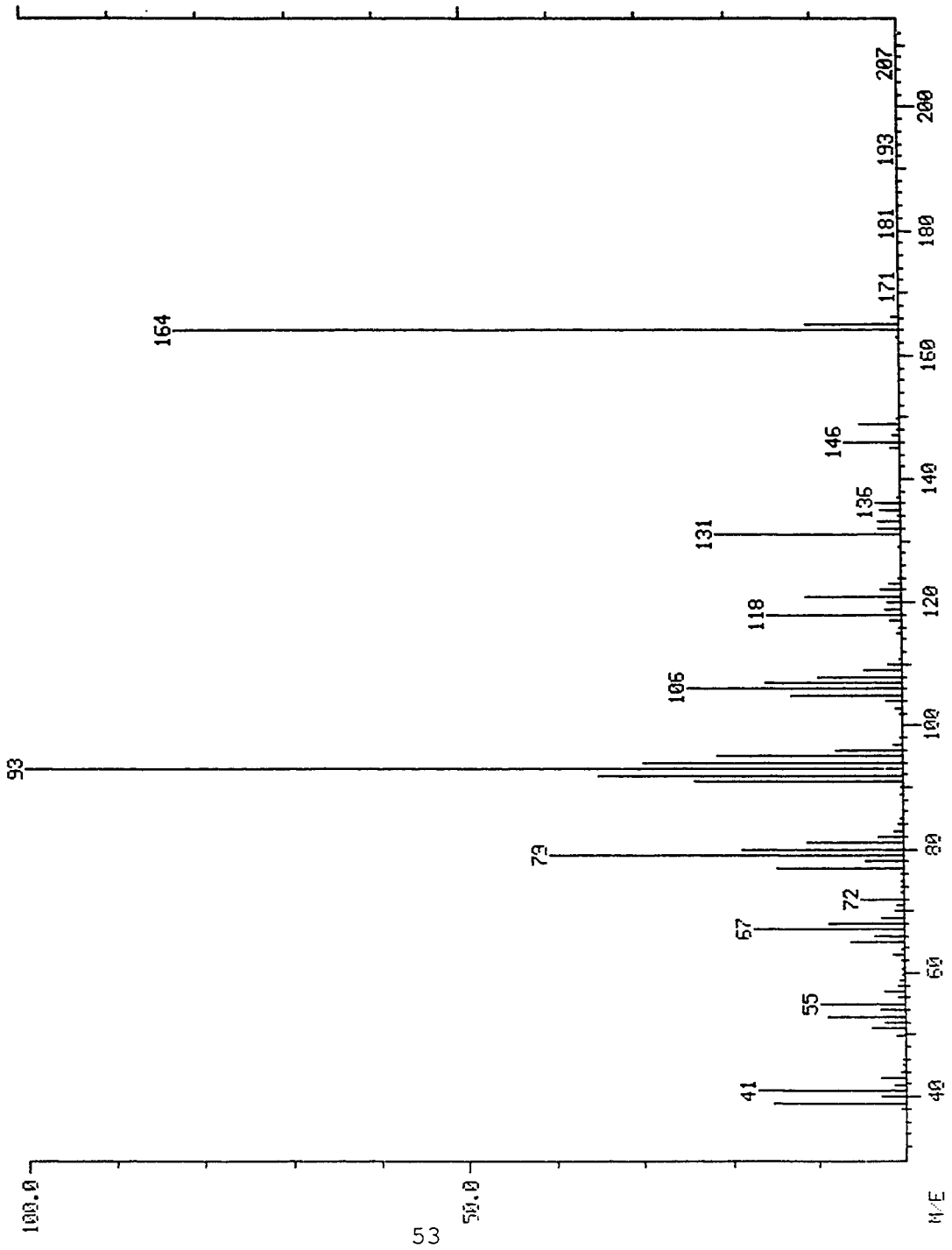


Figure 3: Typical concentration vs. time data for solvolysis of *trans*-4-*t*-butylcyclohexyl tosylate

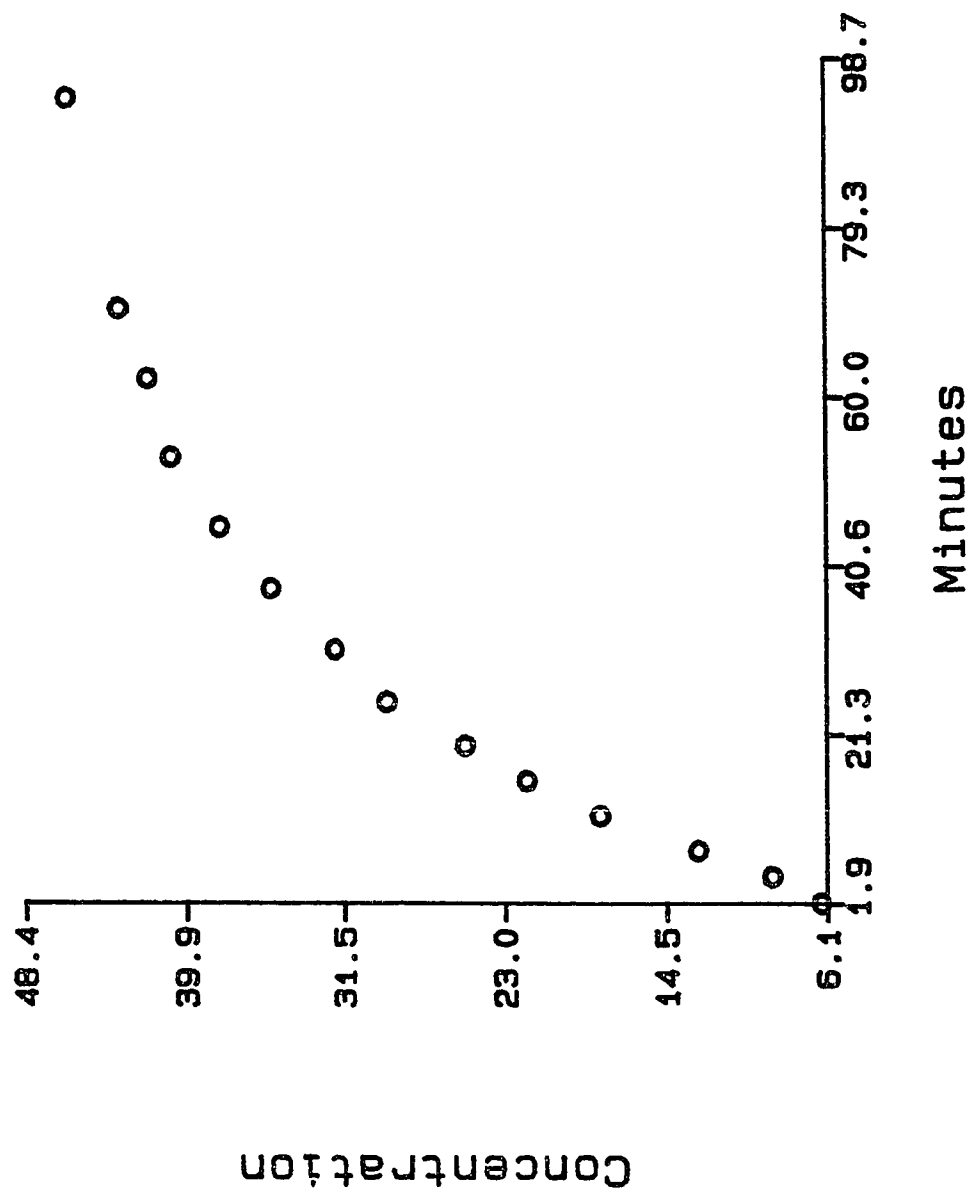


Figure 4: Chromatogram of products from solvolysis of *trans*-4-*t*-butylcyclohexyl tosylate

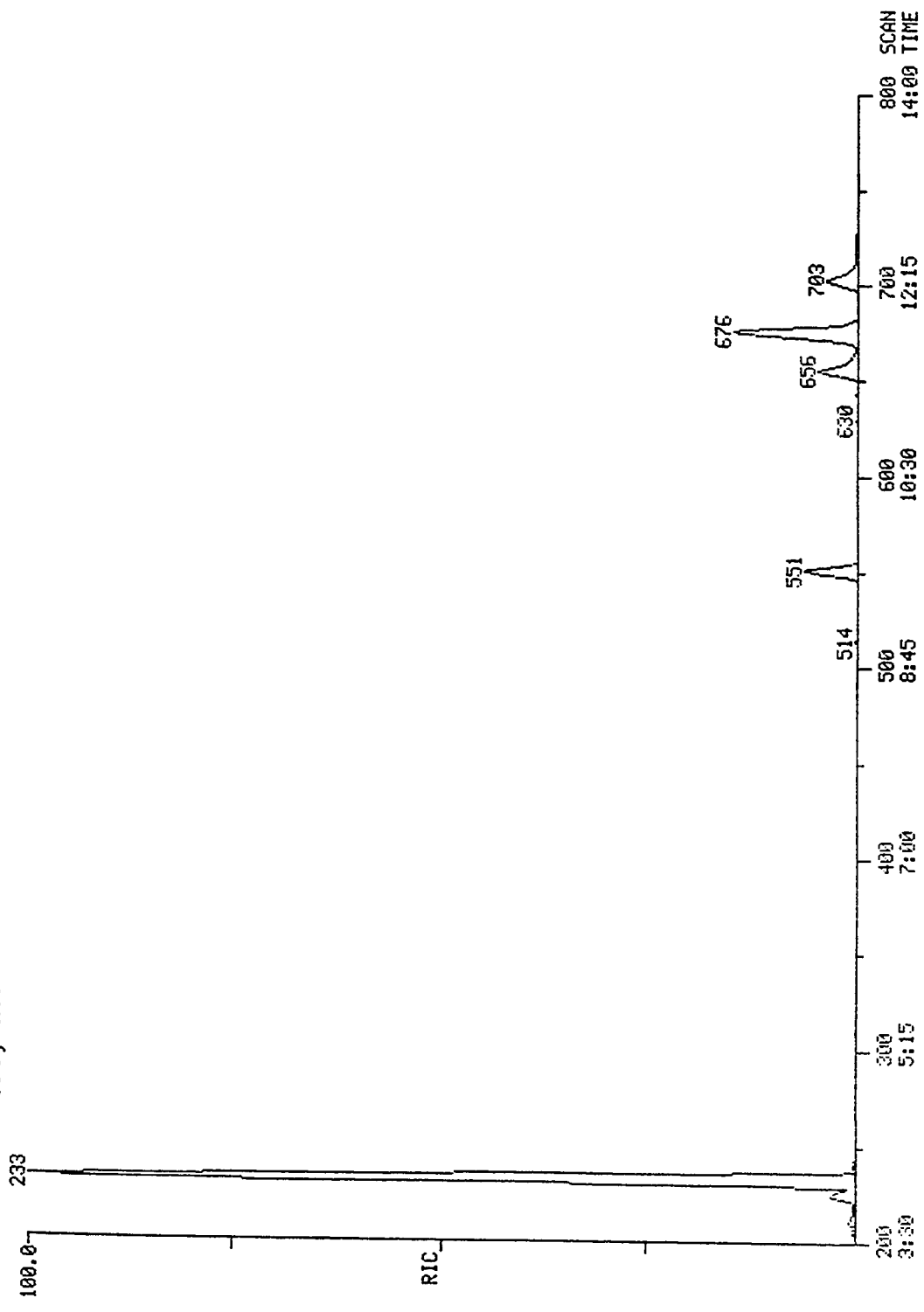


Figure 5: Mass spectrum of 4-*t*-butylcyclohexene

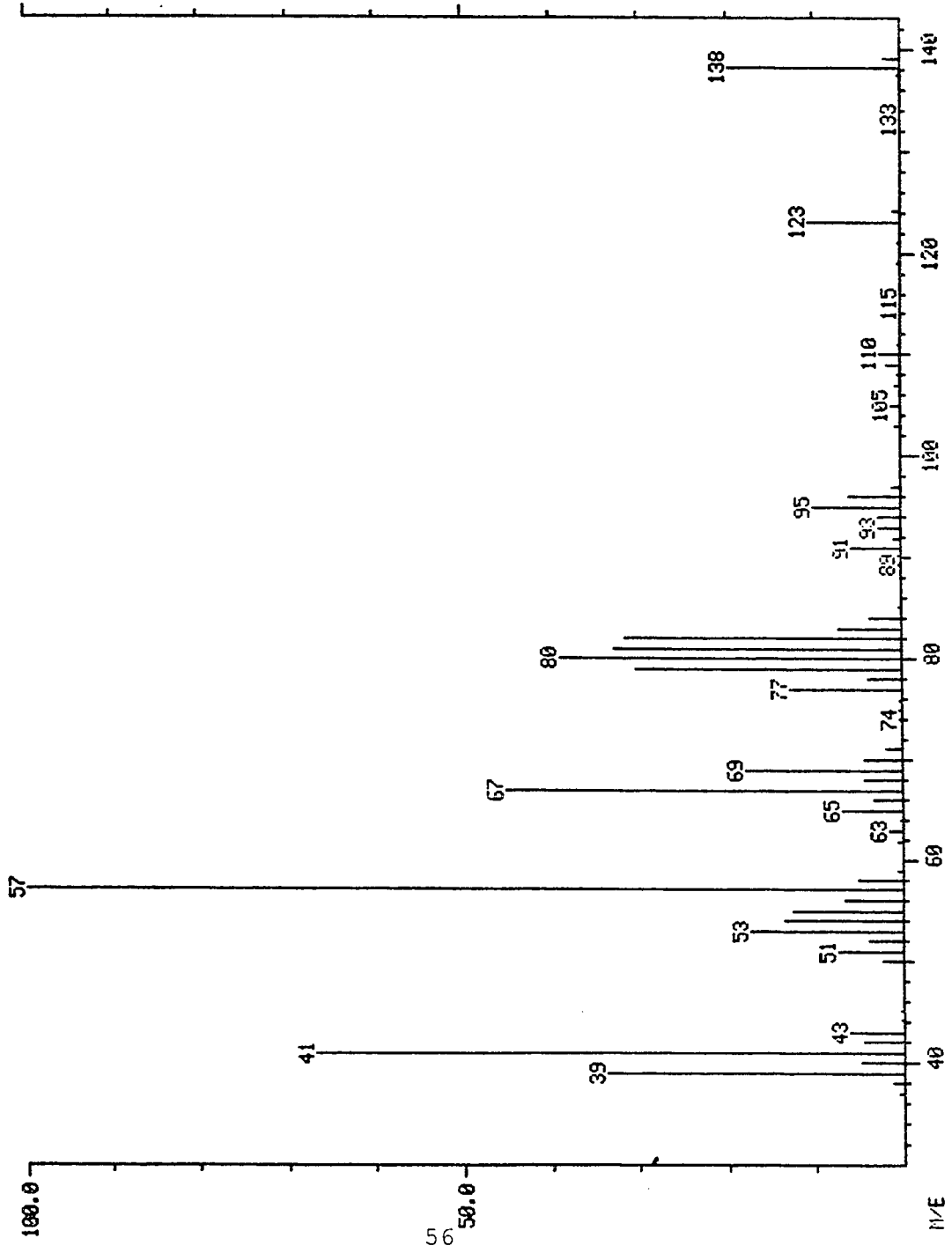


Figure 6: Mass spectrum of *trans*-4-*t*-butylcyclohexyl ethyl ether

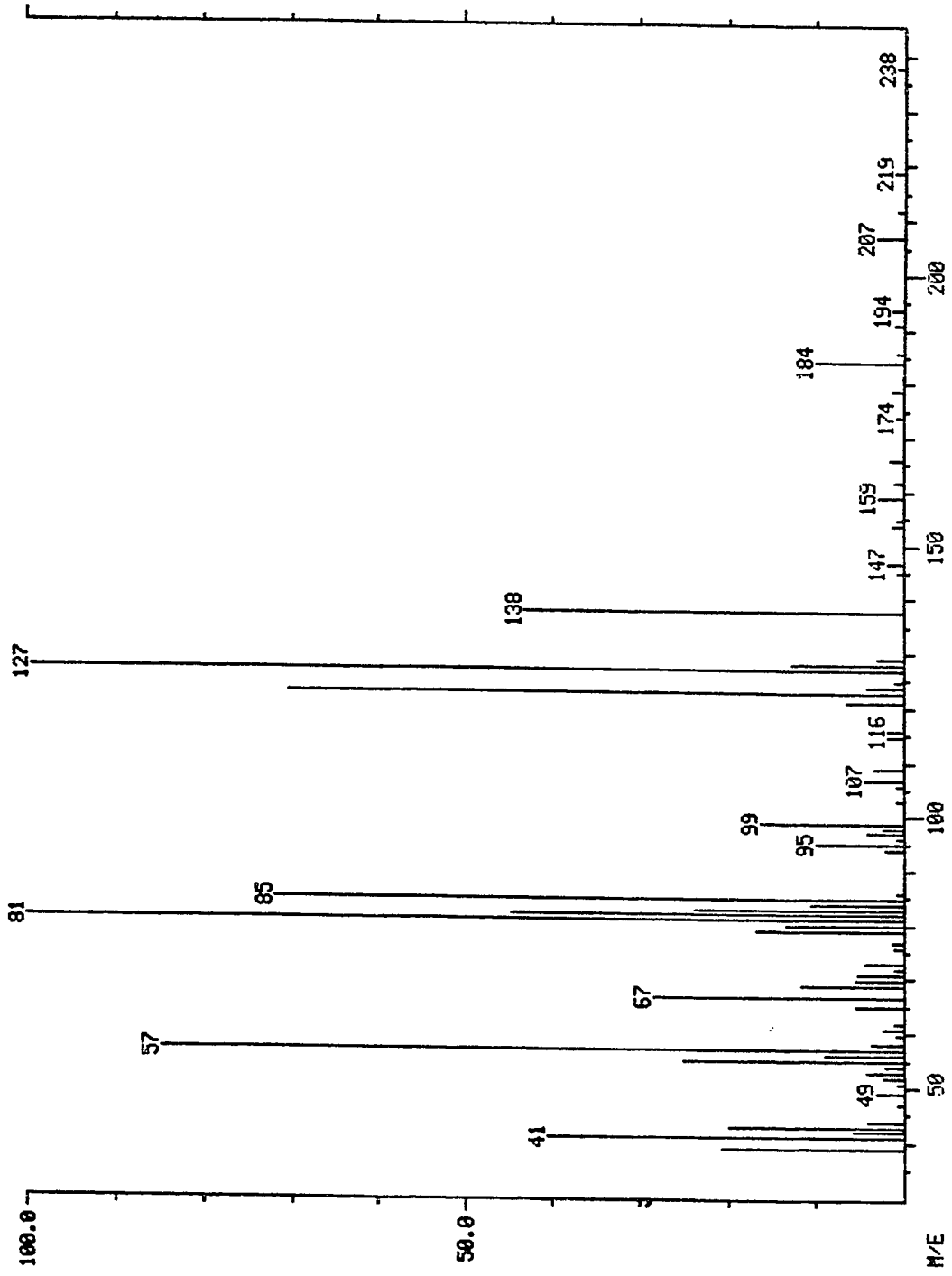


Figure 7: Mass spectrum of *trans*-4-*t*-butylcyclohexyl trifluoroethyl ether

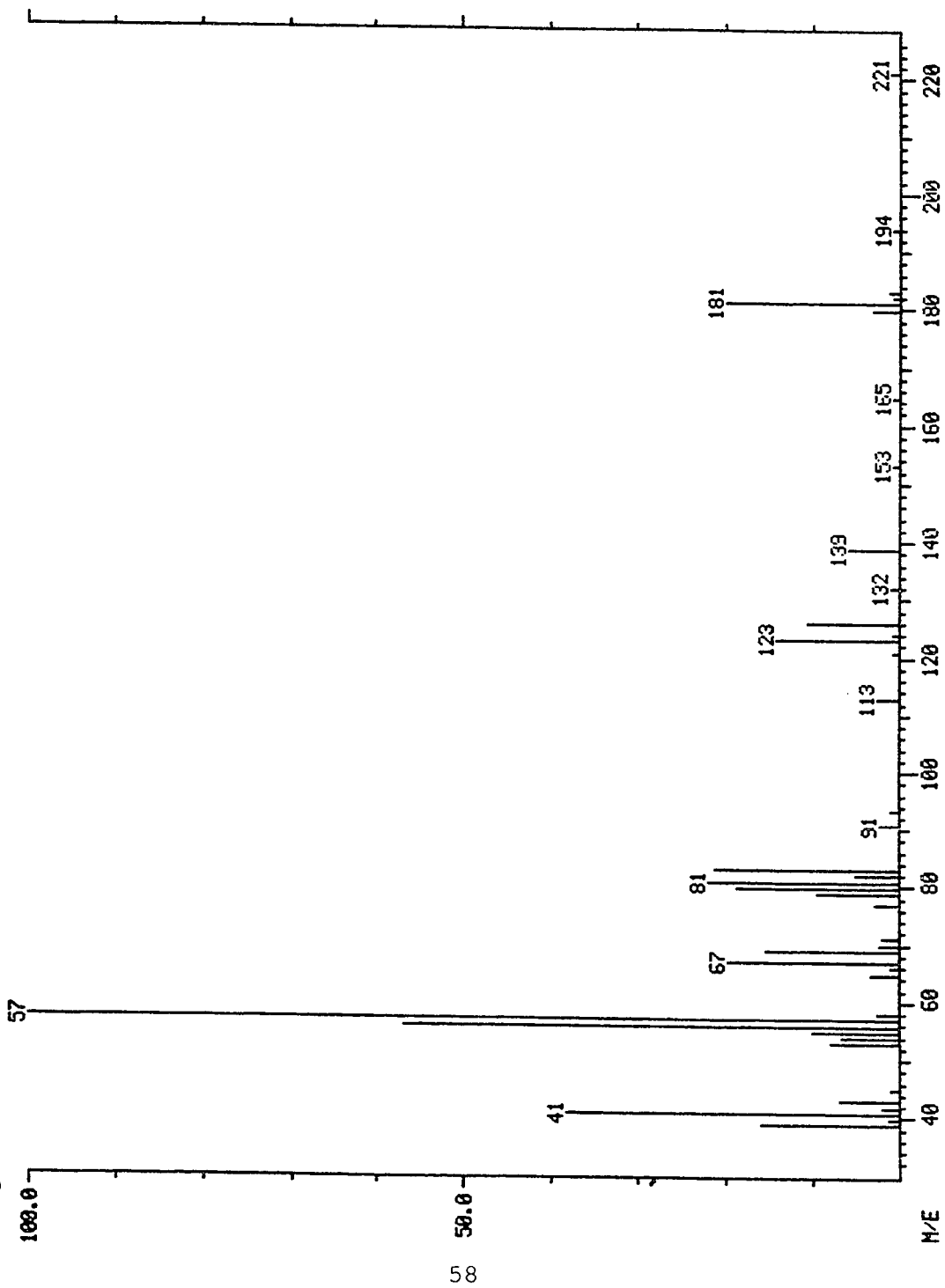


Figure 8: Mass spectrum of *cis*-4-*t*-butylcyclohexyl ethyl ether

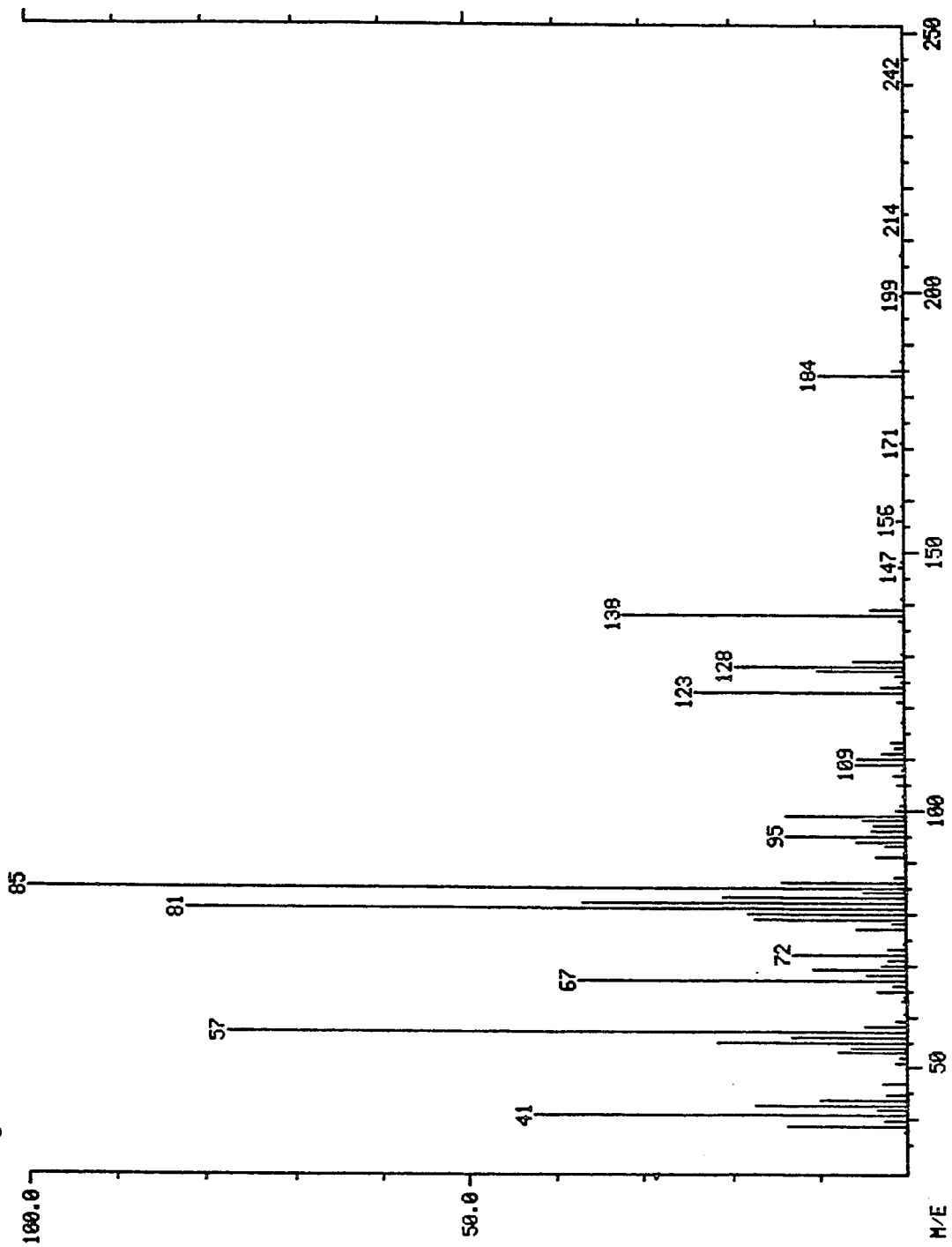


Figure 9: Mass spectrum of *cis*-4-*t*-butylcyclohexyl trifluoroethyl ether

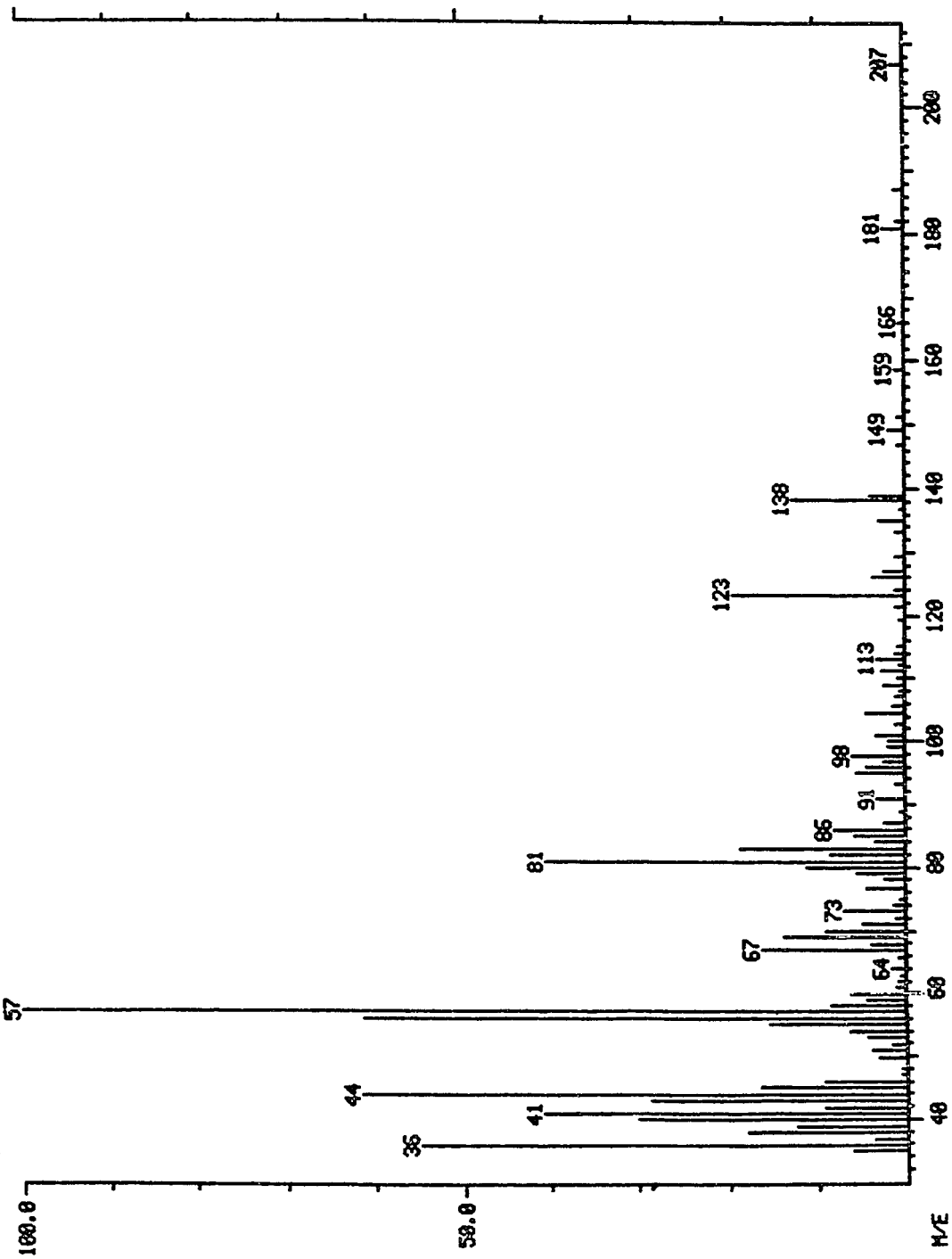




Figure 10: Product ratio vs. solvent ratio for 1-adamantyl tosylate in EtOH/TFE

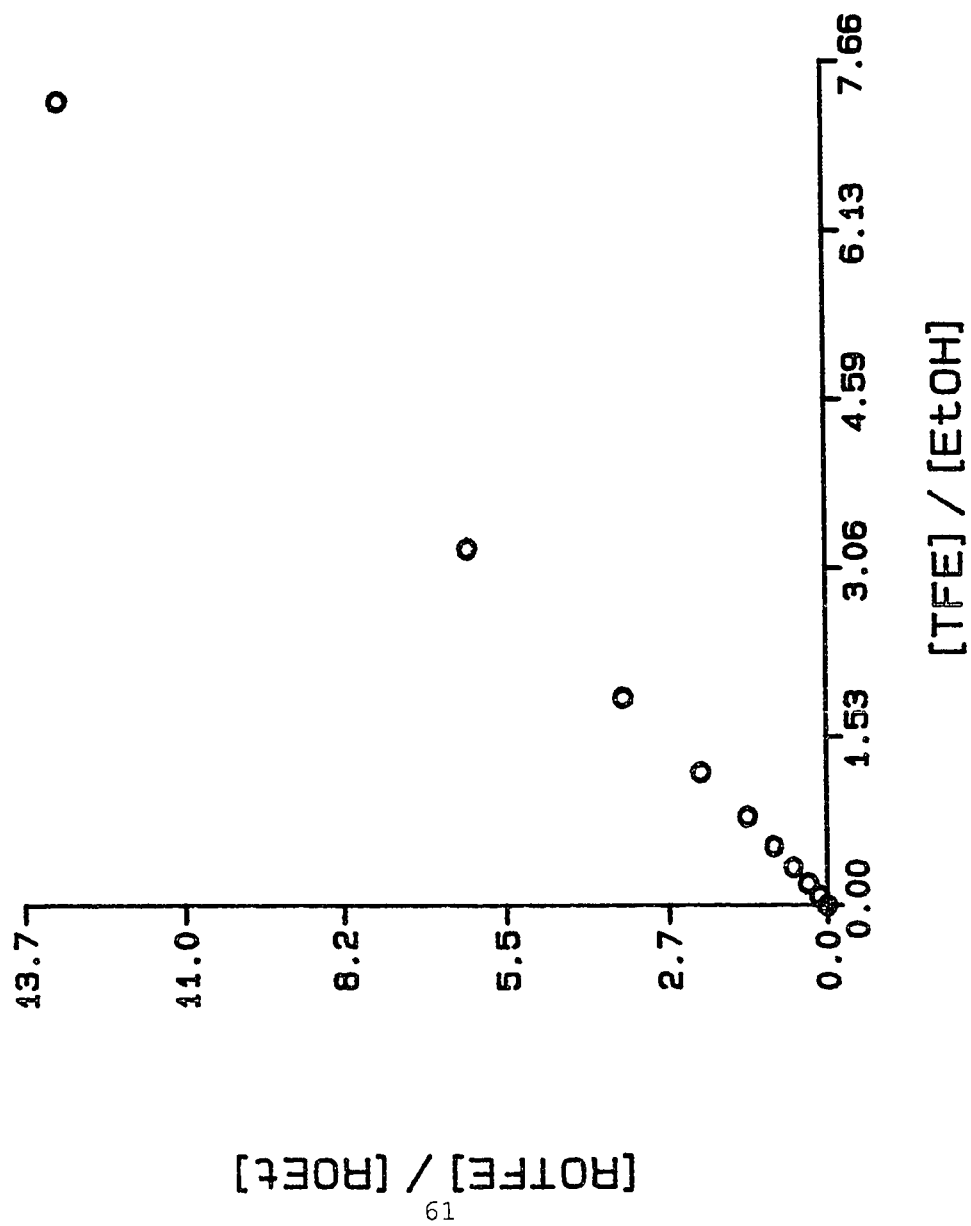


Figure 11: Product ratio vs. solvent ratio for 2-adamantyl tosylate in EtOH/TFE

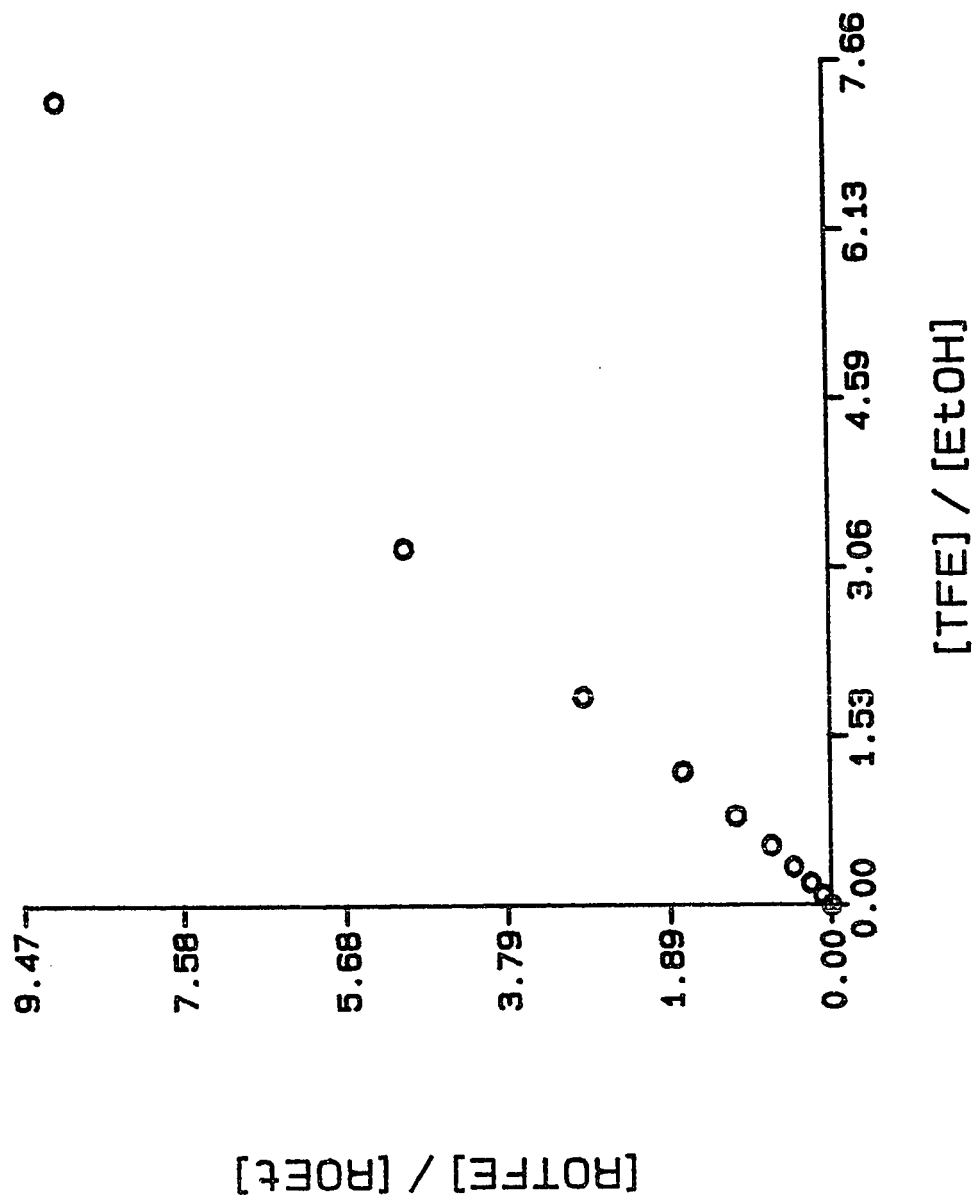


Figure 12: Combined products ratio vs. solvent ratio for *trans*-4-*t*-butylcyclohexyl tosylate

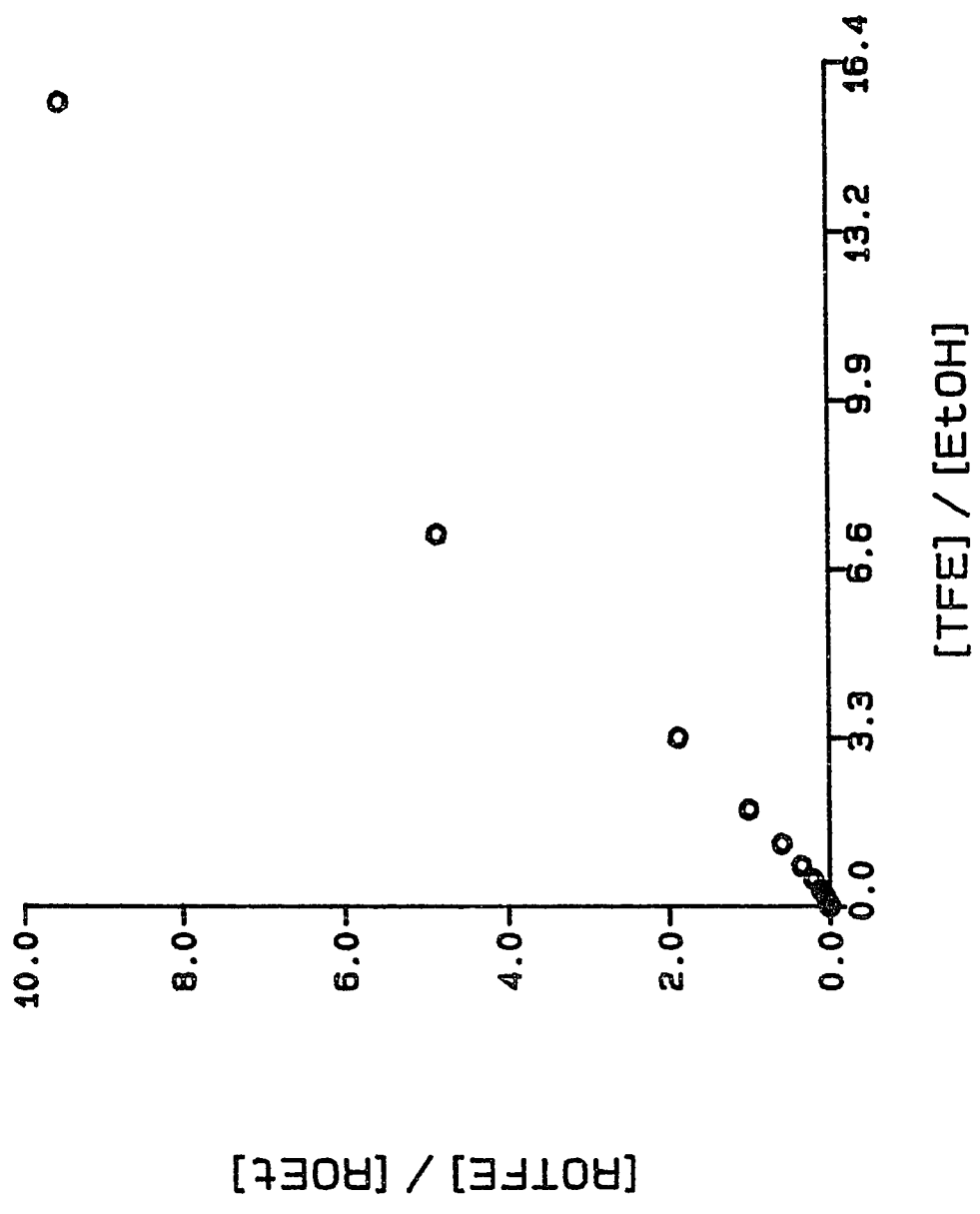


Figure 13: Excess 1-adamantyl trifluoroethyl ether vs. mole fraction trifluoroethanol

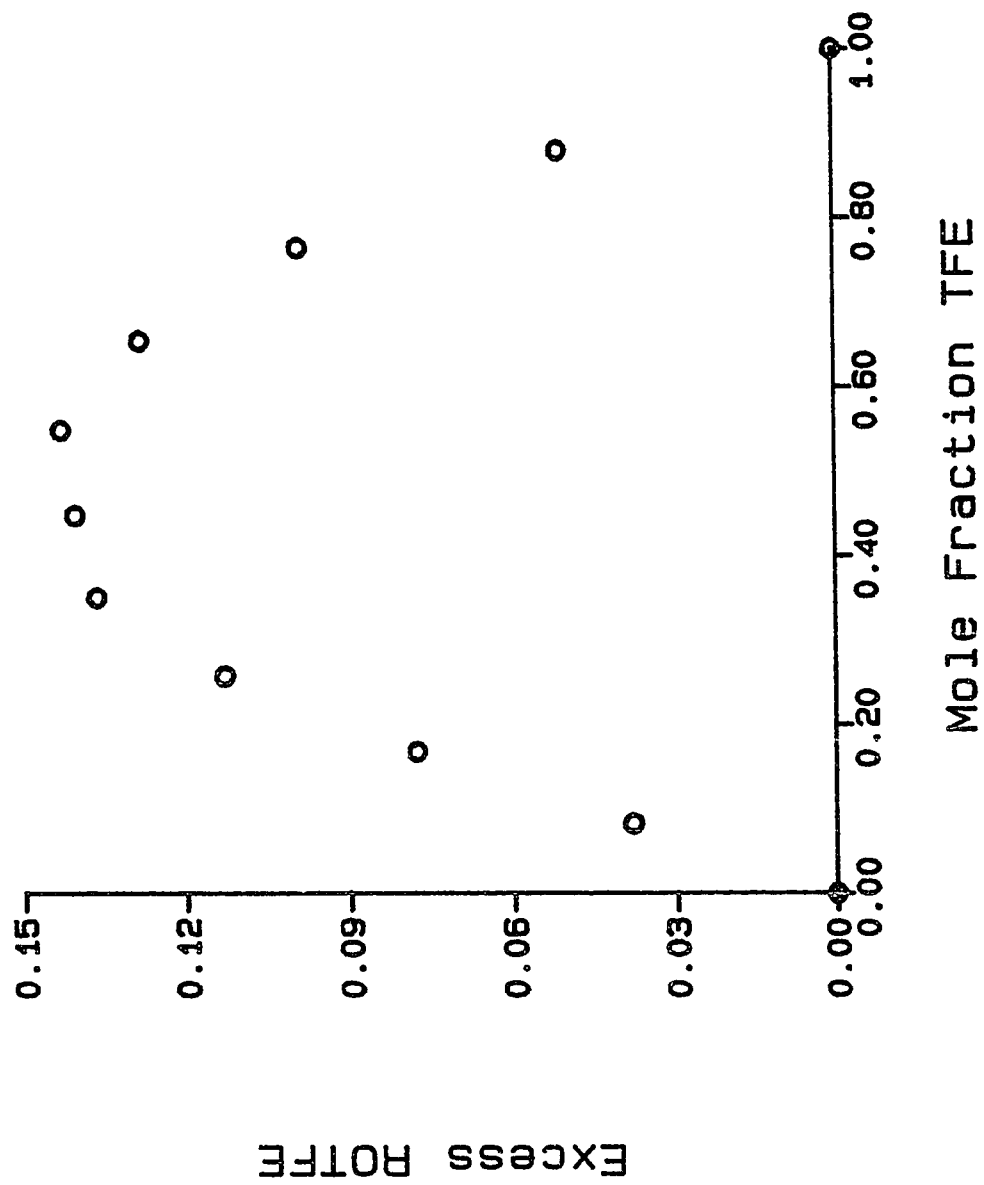


Figure 14: Excess 2-adamantyl trifluoroethyl ether vs. mole fraction trifluoroethanol

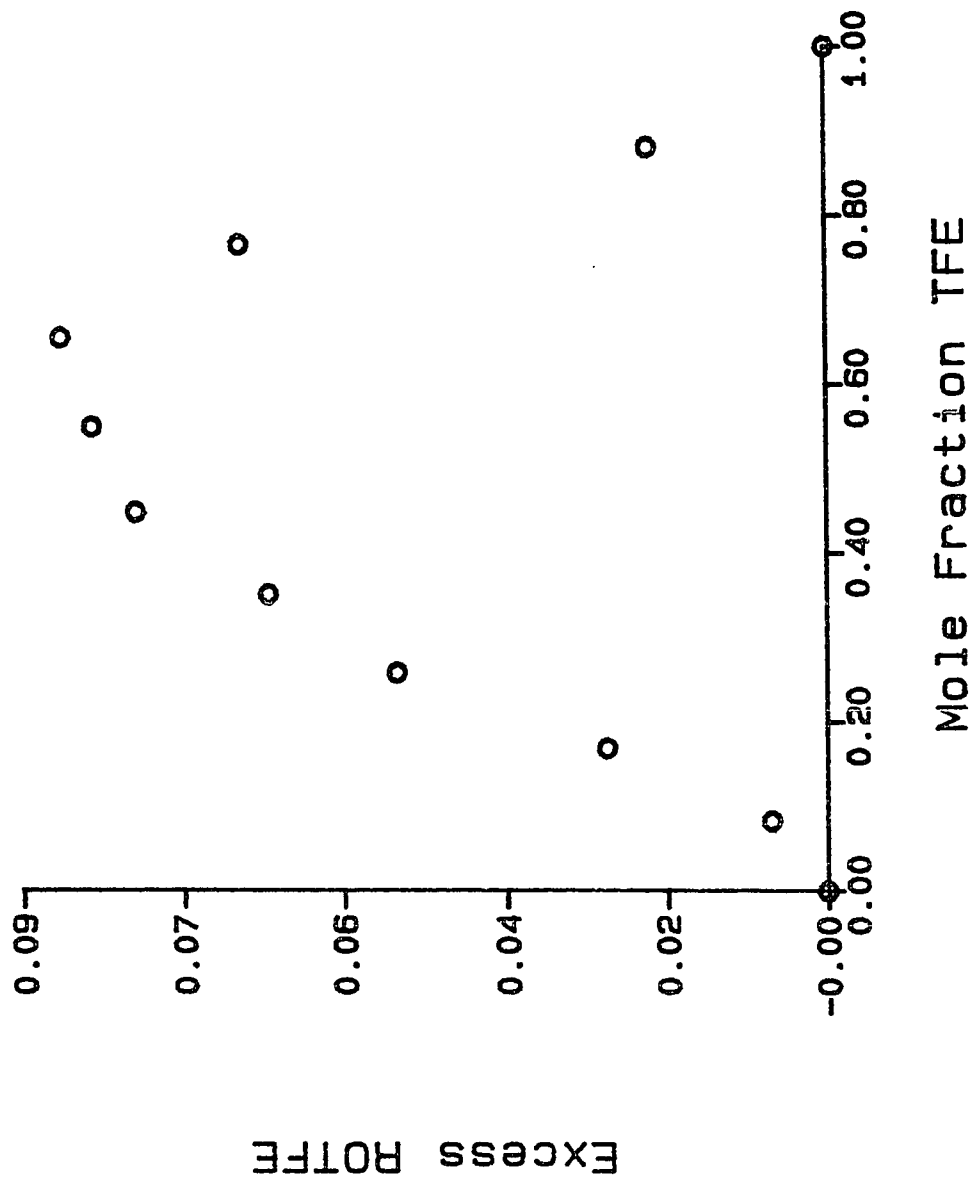


Figure 15: Excess backside 2-adamantyl trifluoroethyl ether vs. mole fraction trifluoroethanol

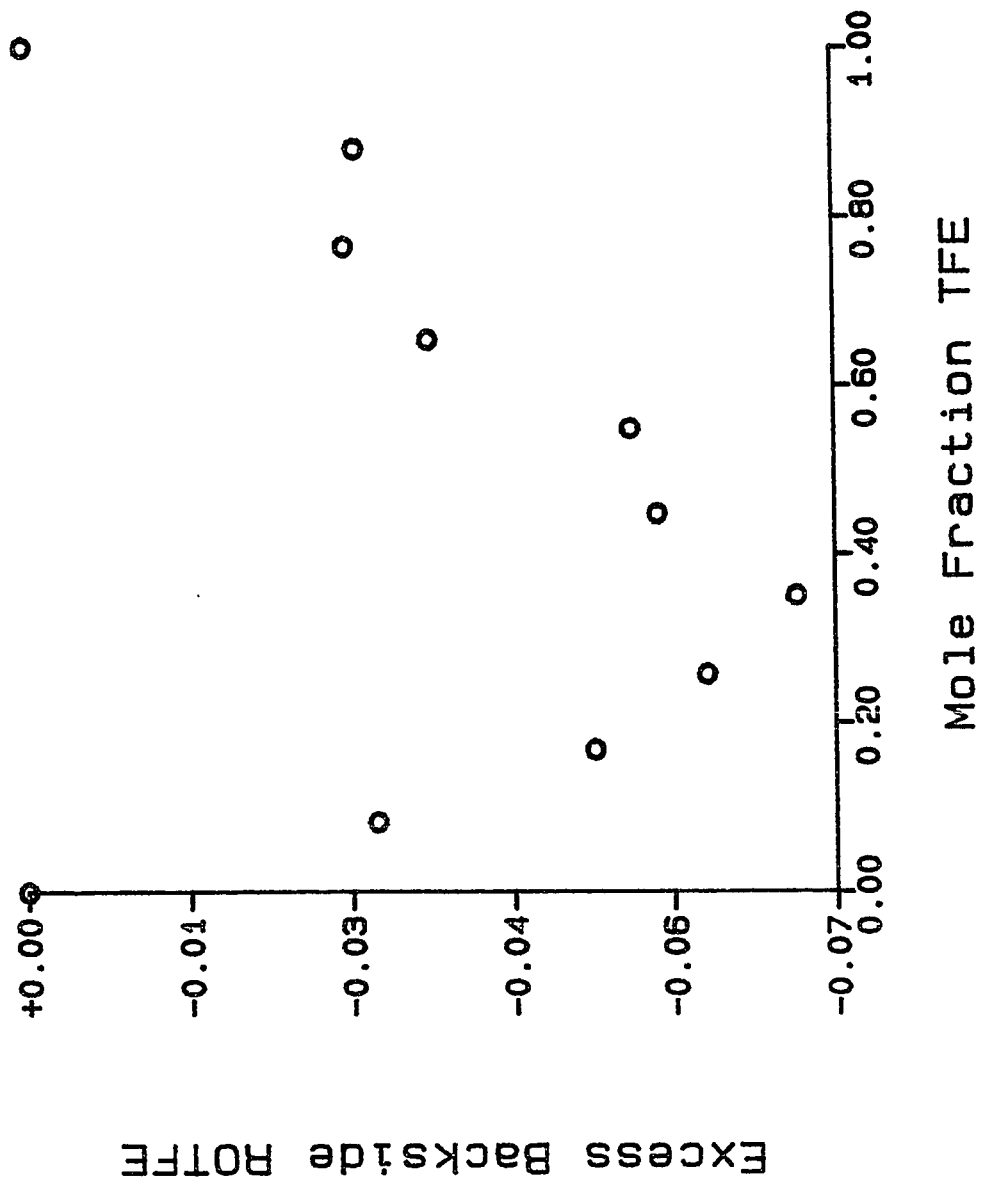


Figure 16: Product ratio vs. solvent ratio for backside reaction in 2-adamantyl tosylate

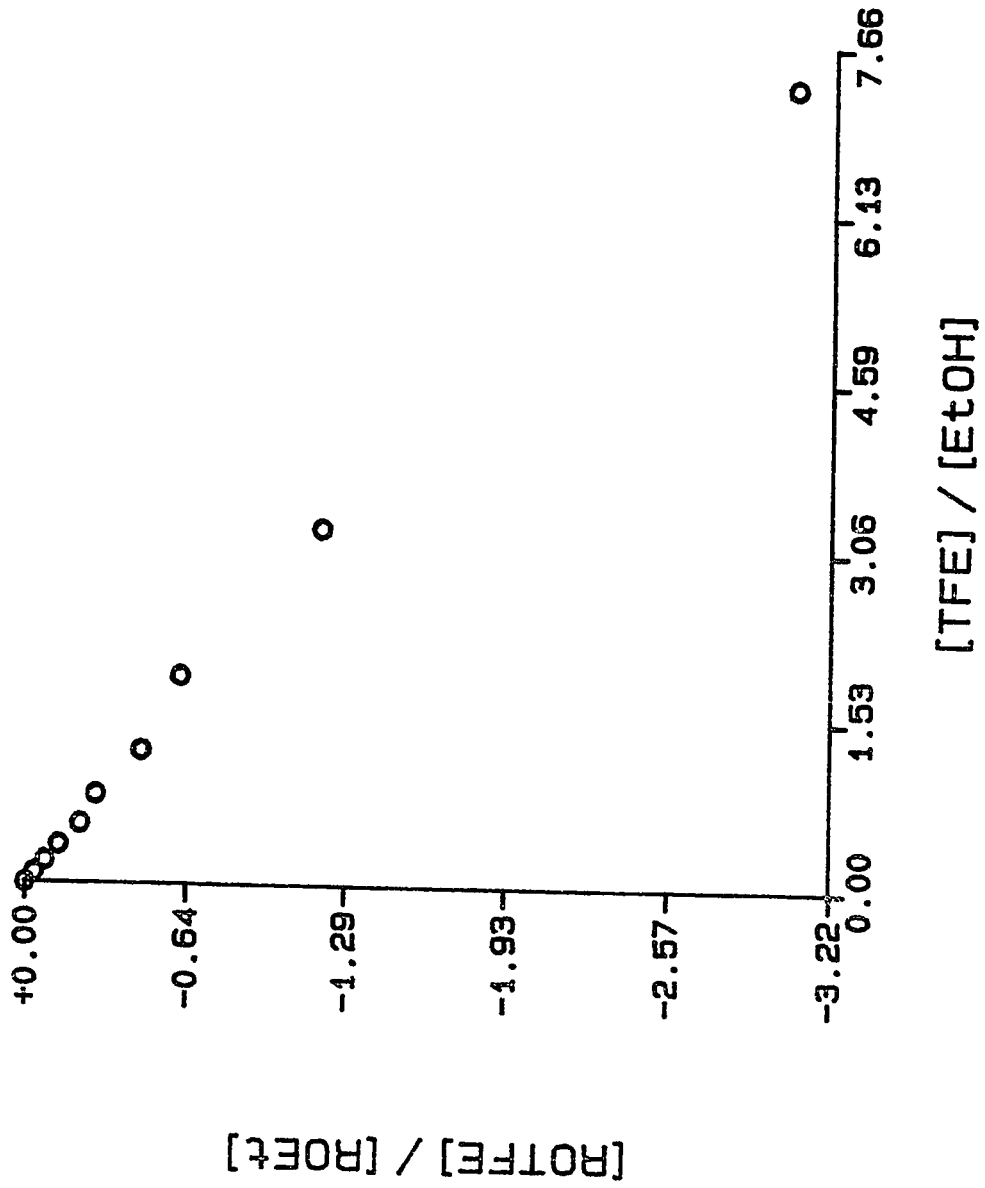


Figure 17: Product ratio vs. solvent ratio for frontside reaction for *trans*-4-*t*-butylcyclohexyl tosylate

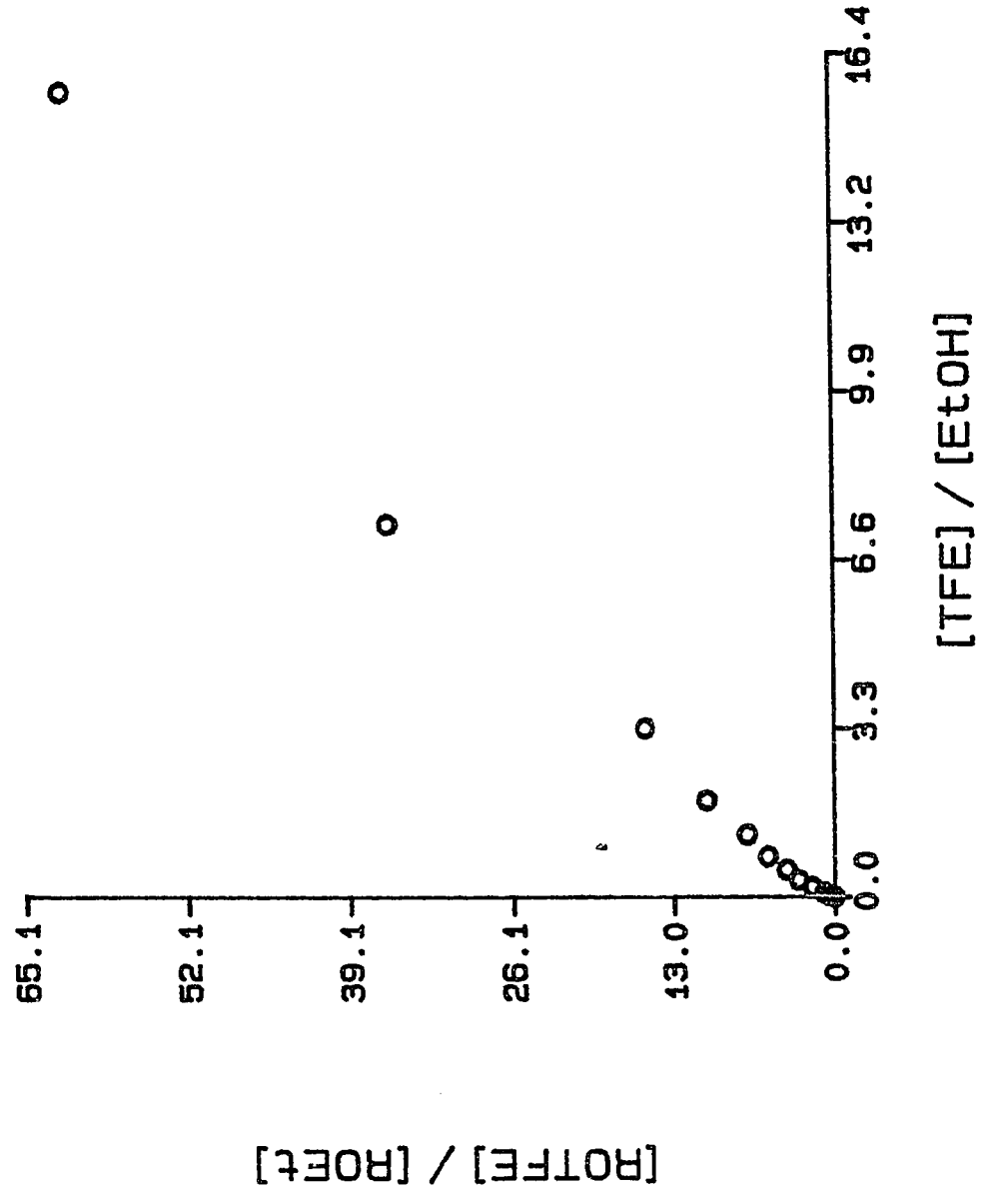




Figure 18: Product ratio vs. solvent ratio for backside reaction for *trans*-4-*t*-butylcyclohexyl tosylate

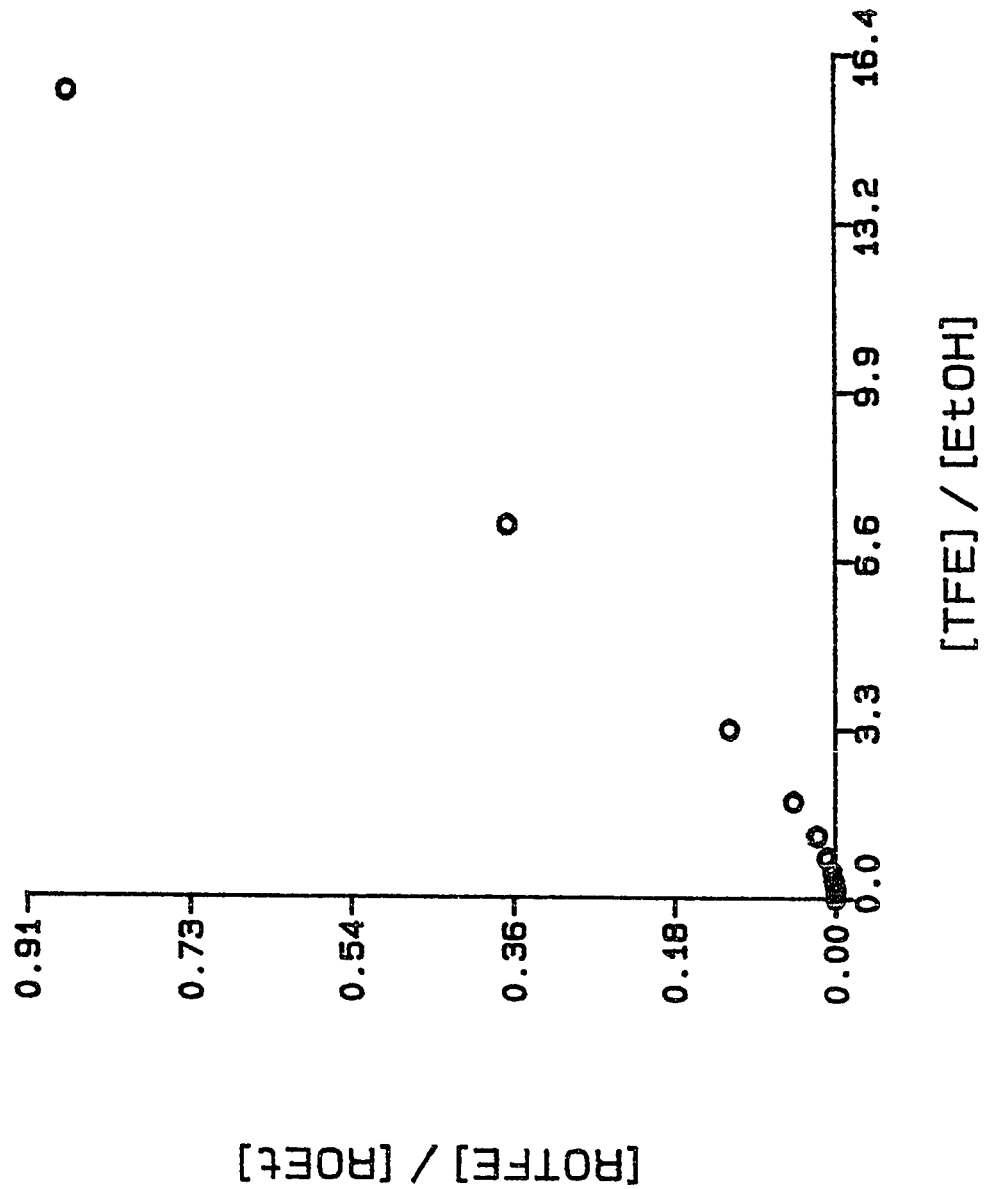


Figure 19: Elimination vs. mole fraction ethanol in *trans*-4-*t*-butylcyclohexyl tosylate

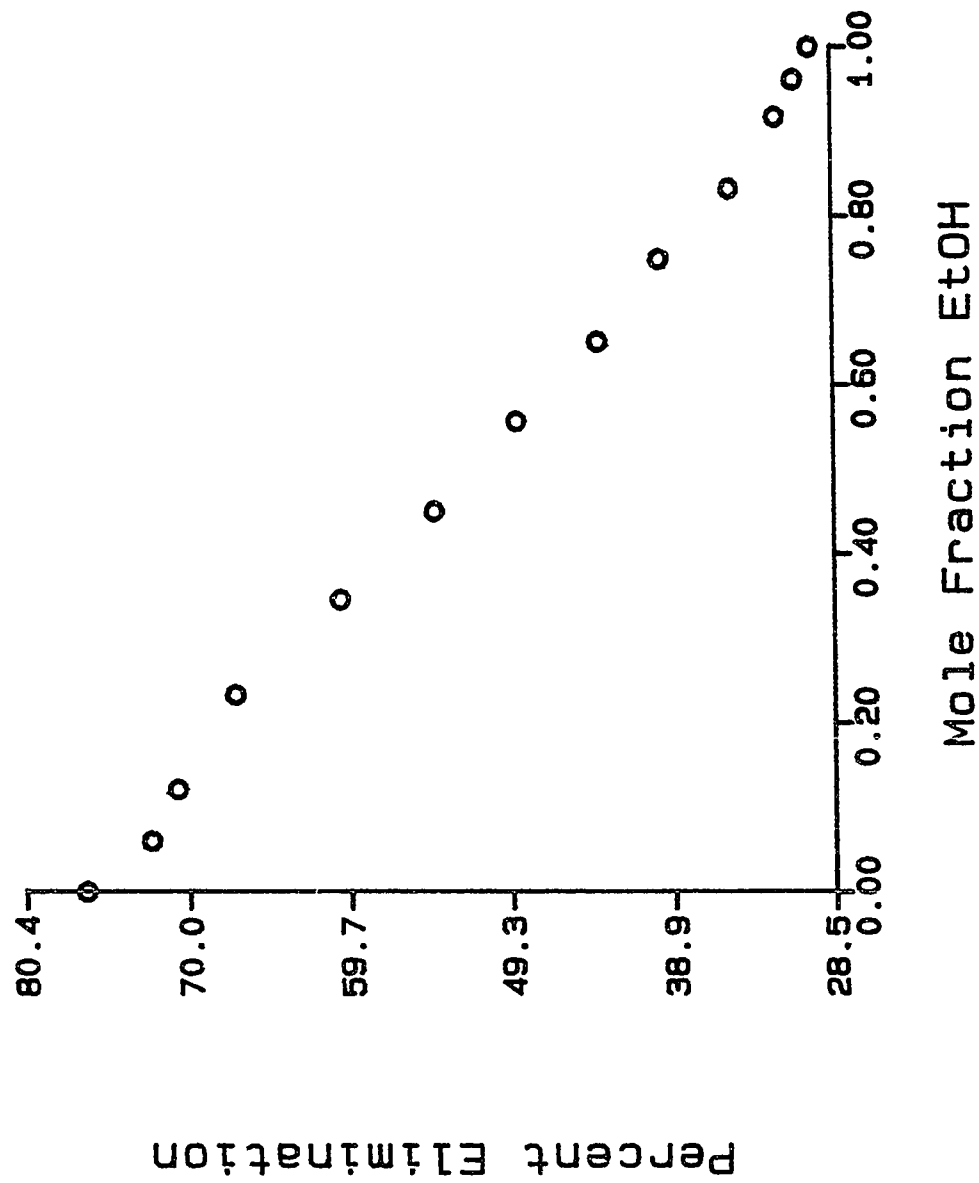


Figure 20: Log rate vs. mole fraction trifluoroethanol for *trans*-4-*t*-butylcyclohexyl tosylate

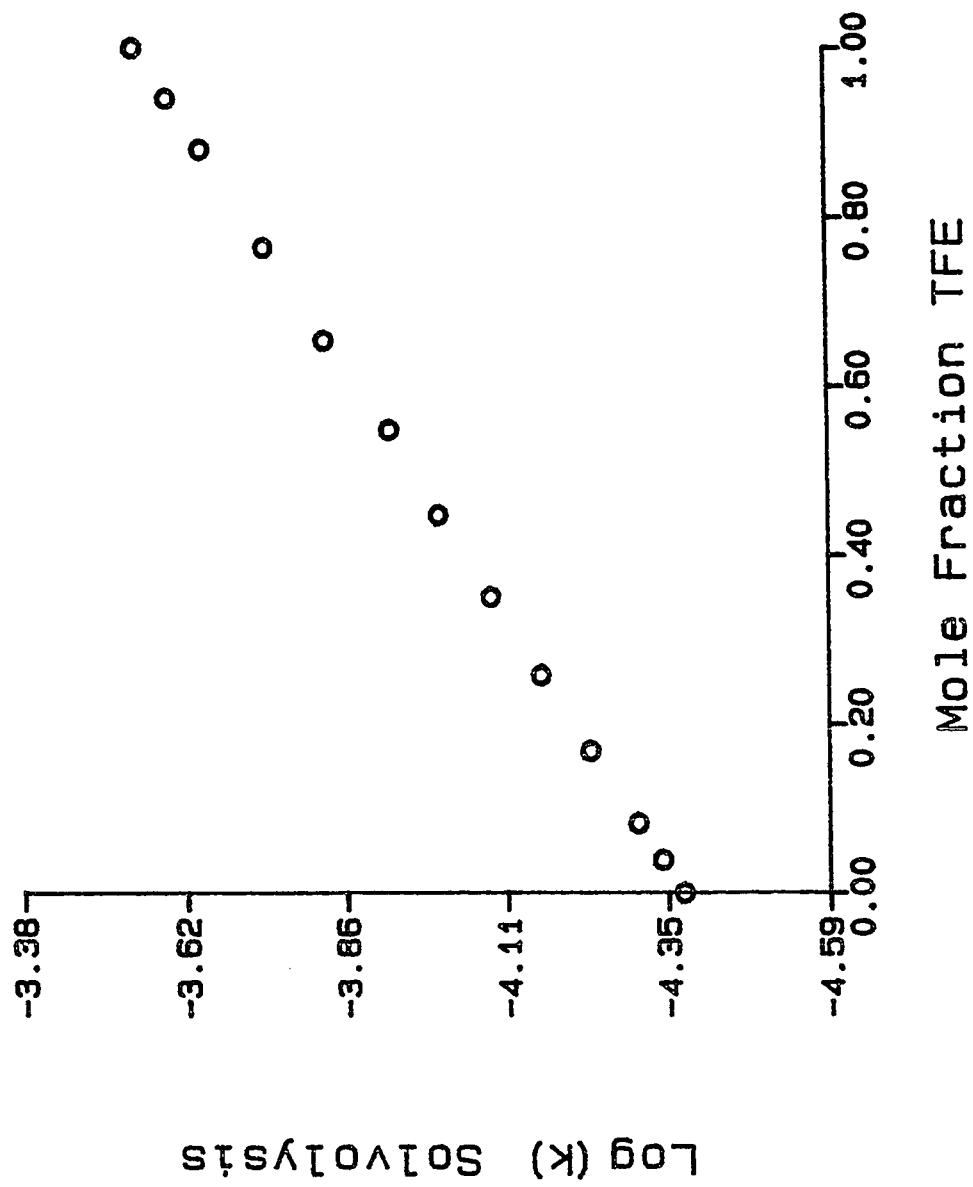


Figure 21: Log rate of formation for 4-*t*-butylcyclohexene vs. mole fraction trifluoroethanol

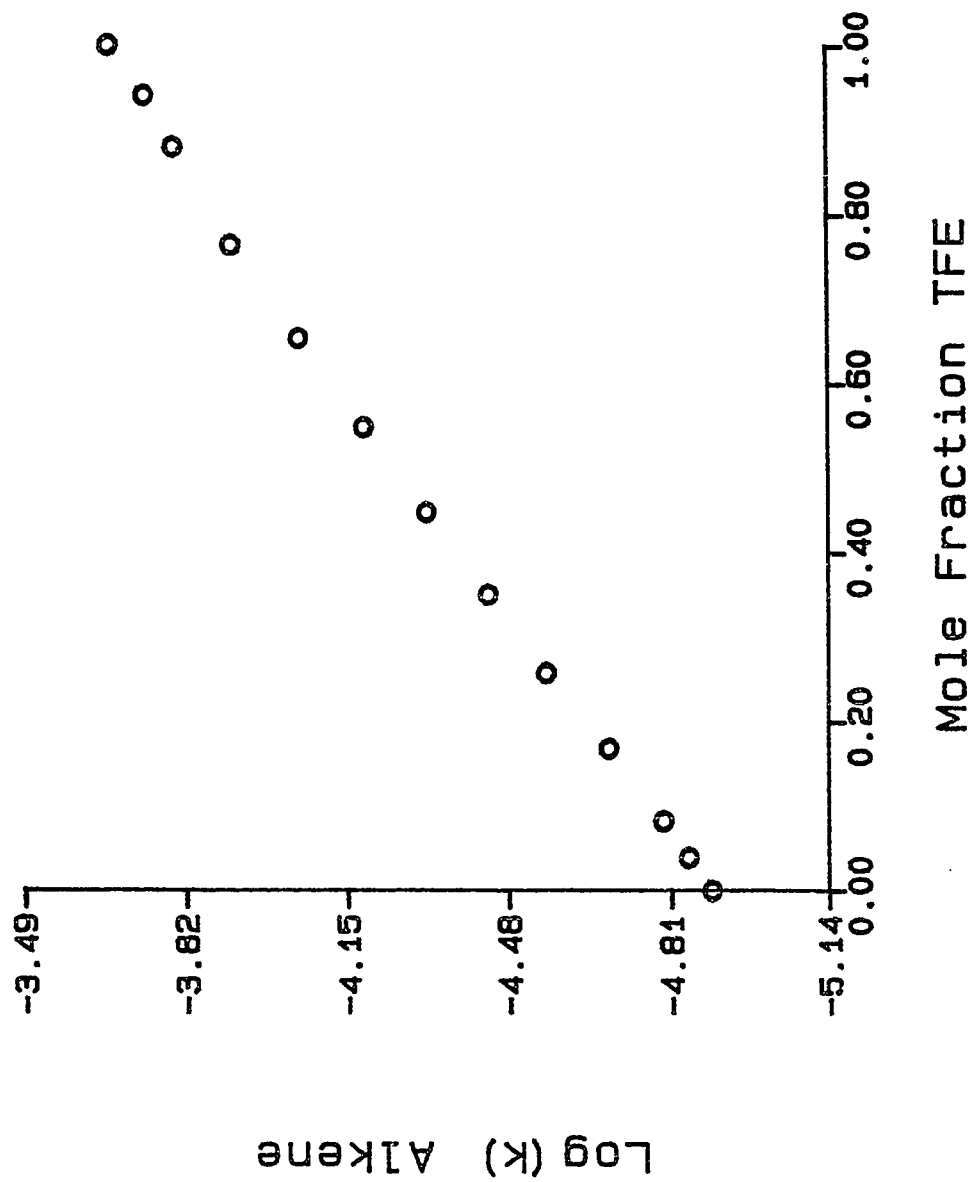


Figure 22: Log rate of formation for *cis*-4-*t*-butylcyclohexyl trifluoroethyl ether vs. mole fraction trifluoroethanol

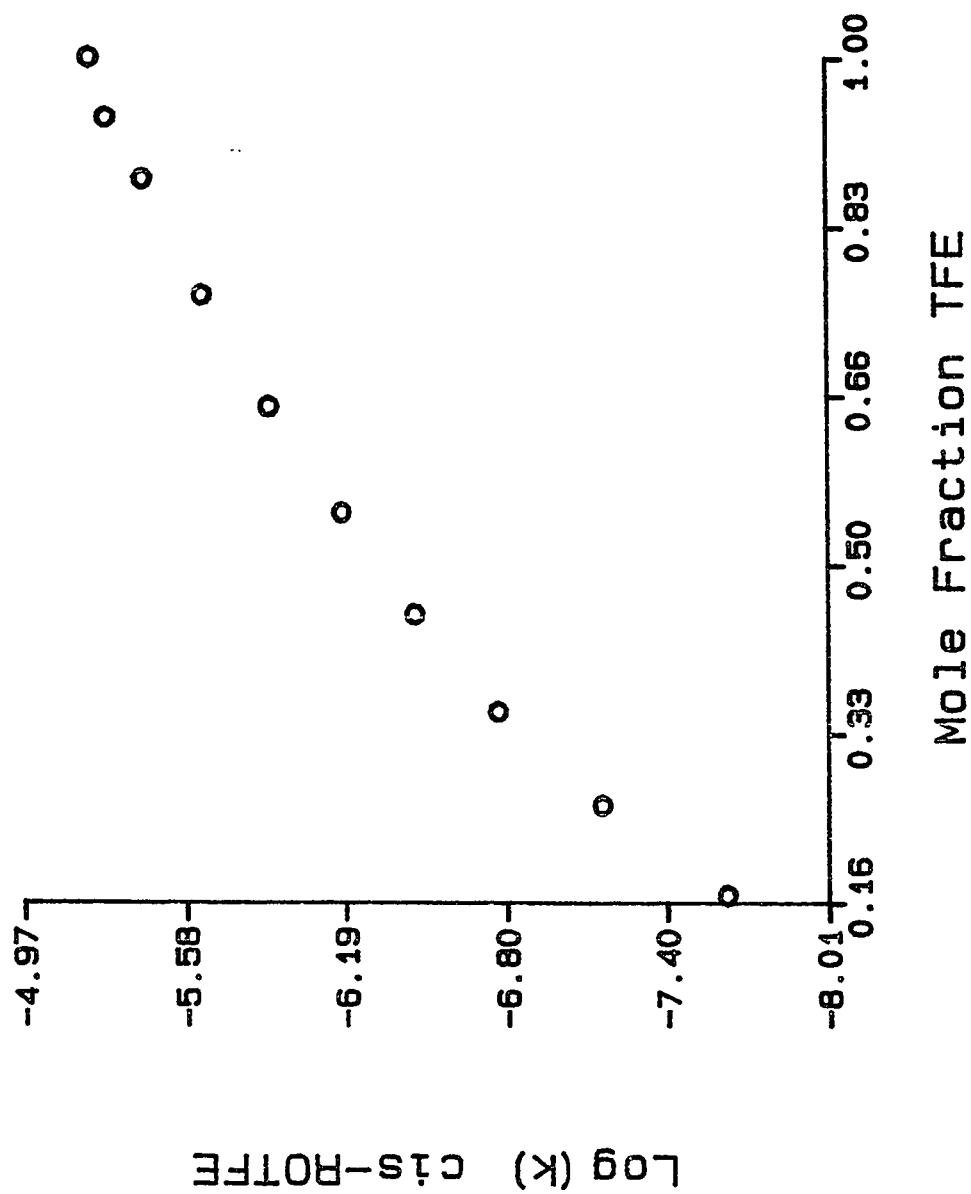


Figure 23: Log rate of formation for *trans*-4-*t*-butylcyclohexyl trifluoroethyl ether vs. mole fraction trifluoroethanol

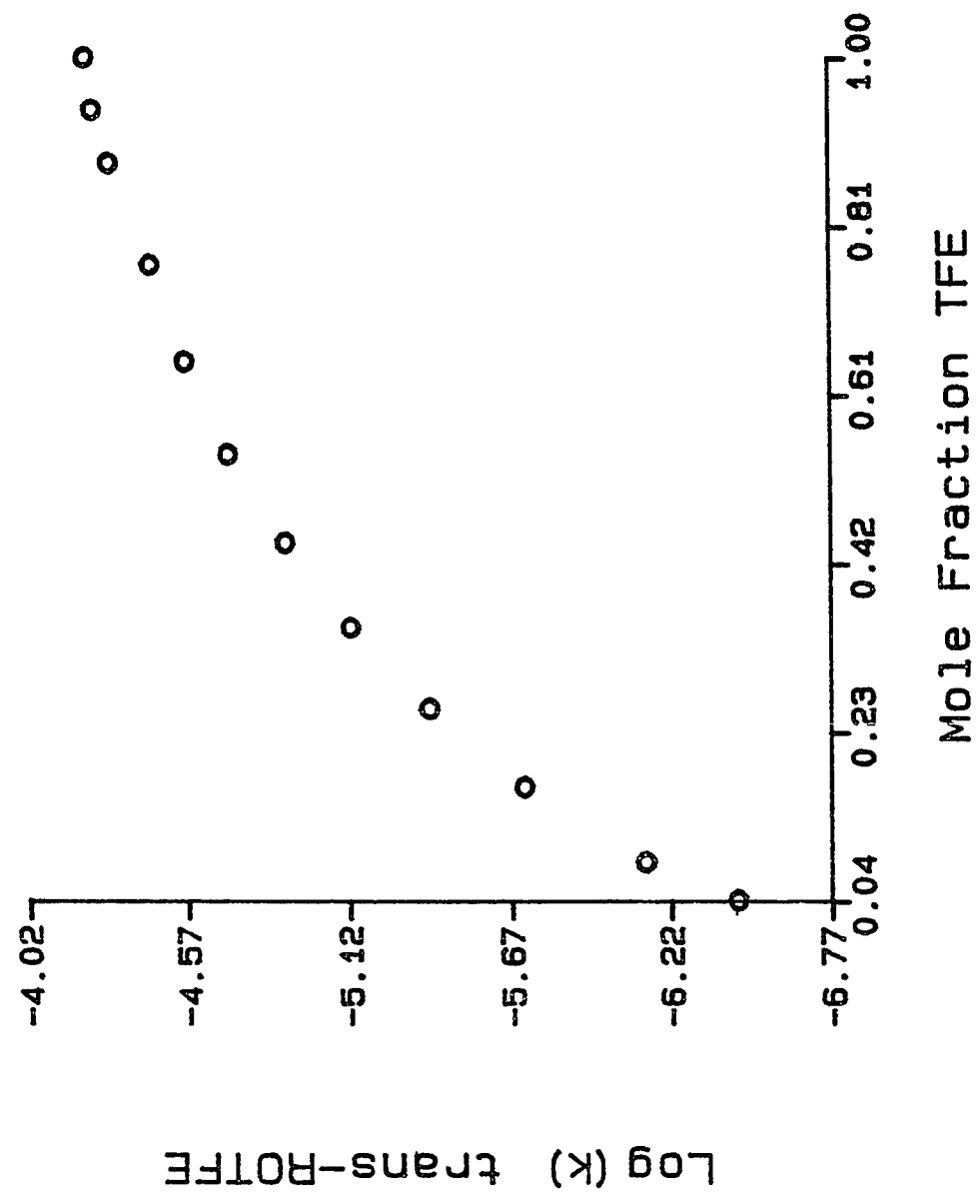


Figure 24: Log rate of formation for *trans*-4-*t*-butylcyclohexyl ethyl ether vs. mole fraction trifluoroethanol

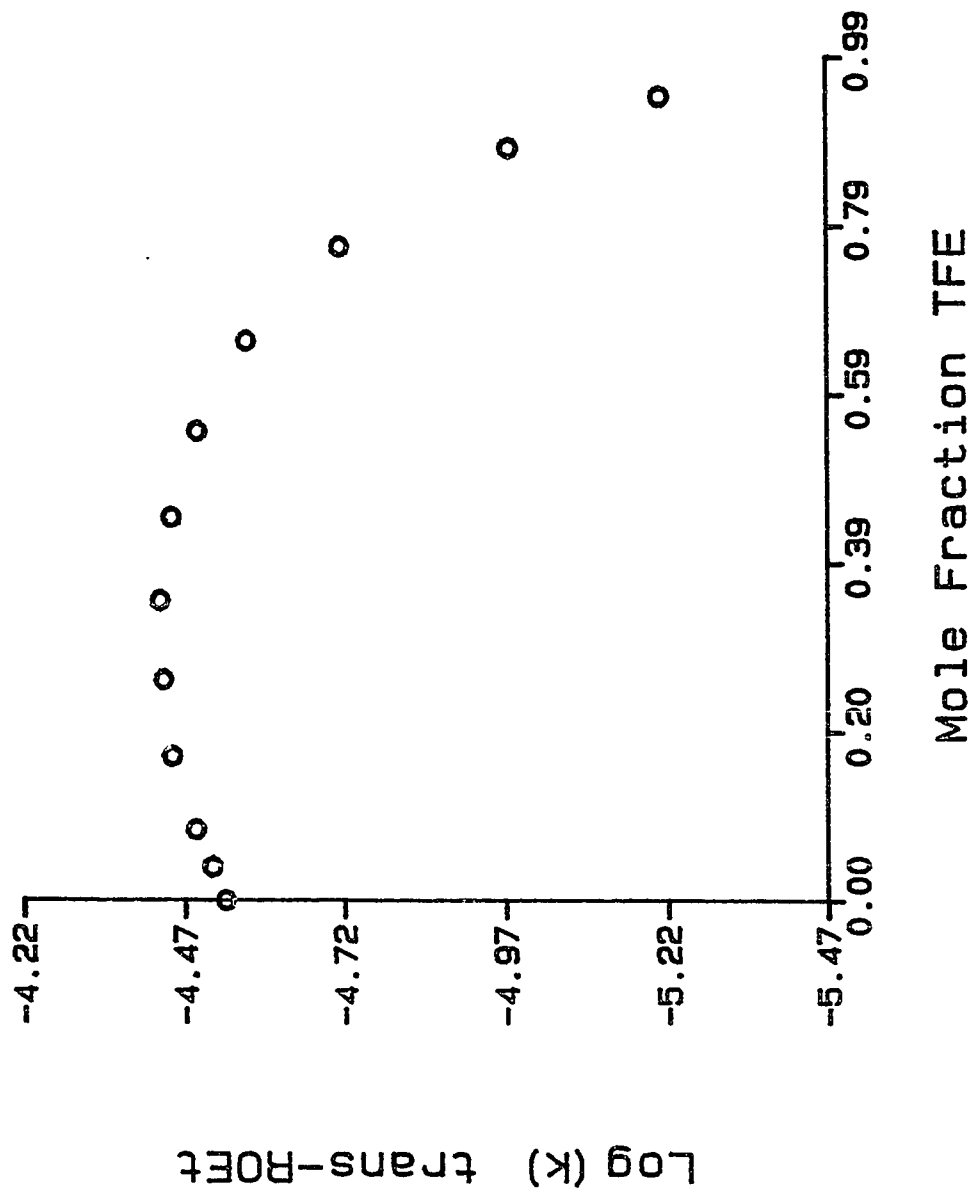


Figure 25: Log rate of formation for *cis*-4-*t*-butylcyclohexyl ether vs. mole fraction trifluoroethanol

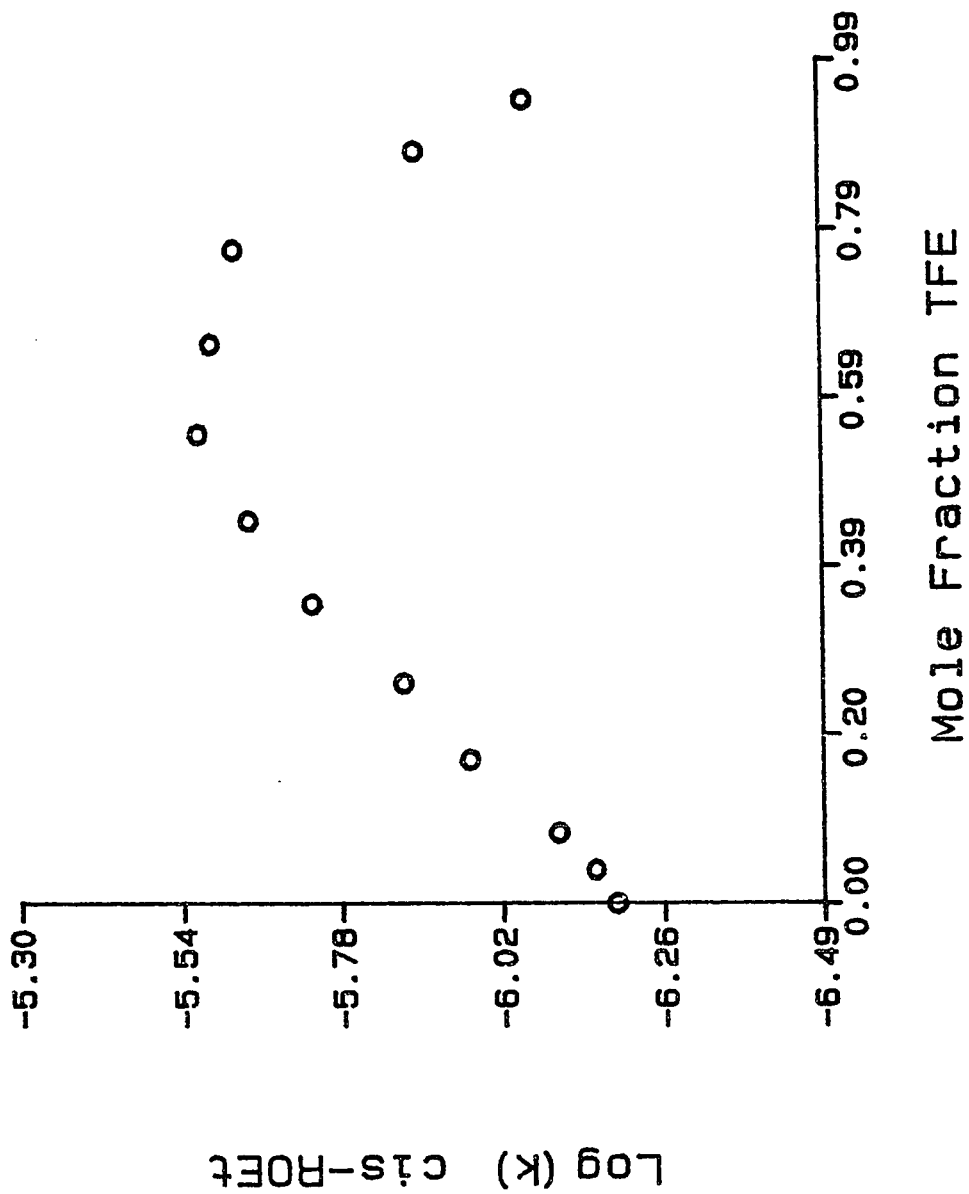




Figure 26: Solvolysis products of 1-bicyclo[2,2,1]heptan carbonyl tosylate vs. temperature

