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Solvolysis of 1-t-butylvinyl trifluoromethanesulfonate

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Solvolysis
of
1-*t*-Butylvinyl Trifluoromethanesulfonate

A Thesis
Presented to
The Faculty of the Department of Chemistry
The College of William and Mary in Virginia

In Partial Fulfillment
Of the Requirements for the Degree of
Master of Arts

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by
Barbara L. Gross
1983

APPROVAL SHEET

This thesis is submitted in partial fulfillment of
the requirements for the degree of

MASTER OF ARTS

Barbara L. Gross

Author

Approved, August 1983

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David W. Thompson, Ph.D.

William H Bunnelle

William H. Bunnelle, Ph.D.

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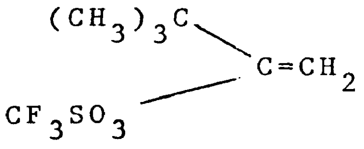
Abstract

The following α-*t*-Butylvinyl trifluoromethansulfonates were synthesized: 3,3-Dimethyl-1-buten-2-yl Triflate (**1**), (*E*)- and (*Z*)- 2-Deuterio-3,3-Dimethyl-1-buten-2-yl Triflate (**2**) and (**3**), and 2,2-Dideuterio-3,3-dimethyl-1-buten-2-yl Triflate (**4**).



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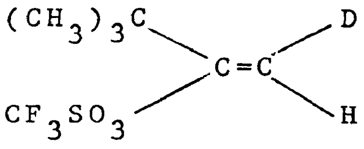

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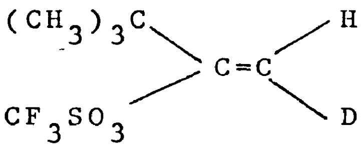

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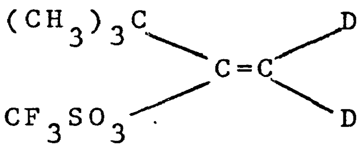


(4)

Analysis of the solvolysis products of these α-*t*-butyl stabilized vinyl cation precursors in 60 vol.% E-W, 70 vol.% E-W, 80 vol.% E-W, 97 wt.% TFE-W solvents permitted a qualitative interpretation of the solvolysis mechanism. The stereochemistry of the trifluoromethanesulfonic acid addition to 3,3-dimethylbutyne is also investigated.

INTRODUCTION

Direct Solvolytic Generation of Vinyl Cations

The most investigated and best understood processes in organic chemistry involve solvolytic displacement reactions at the saturated carbon [1]. With improved leaving groups such as the fluorosulfonate and trifluoromethanesulfonate "super" leaving groups [2],[3] the investigation of solvolytic displacement reactions with simple alkyl vinyl substrates has been realized [1].

Experiments indicating the vinyl cation as an intermediate in solvolytic mechanisms were accomplished within the last 15 years, due to the belief that the vinyl cation was of a much higher energy state relative to trisubstituted carbenium ions. This assumption was said to be confirmed by the low reactivities of simple vinyl halides, even in the presence of silver salts, to undergo (<u>SN1</u>) type reactions [4]. Gas phase thermodynamic data for cations and hydrocarbons can be used to calculate the relative stabilities of the ions [4]. Such a calculation for Figure(1) demonstrates that in the gas phase, the parent vinyl cation is 25 Kcal/mol more stable than the methyl cation and 15 Kcal/mol less stable than the ethyl cation.

$$R_1^+ + R_2H \longrightarrow R_1H + R_2^+$$

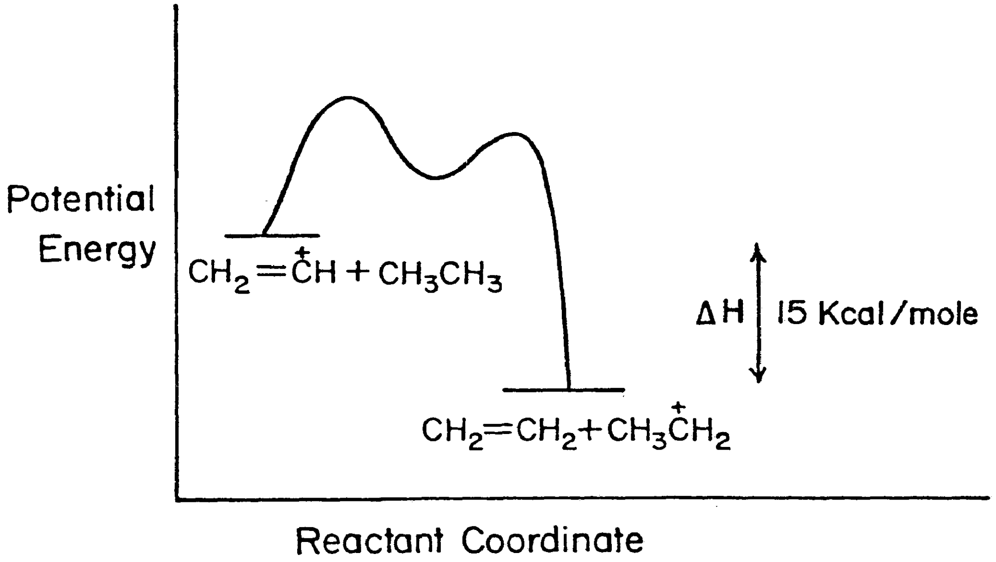
R_2H; CH_4 or CH_3CH_3 R_2^+; $\overset{+}{C}H_3$ or CH_3CH_2

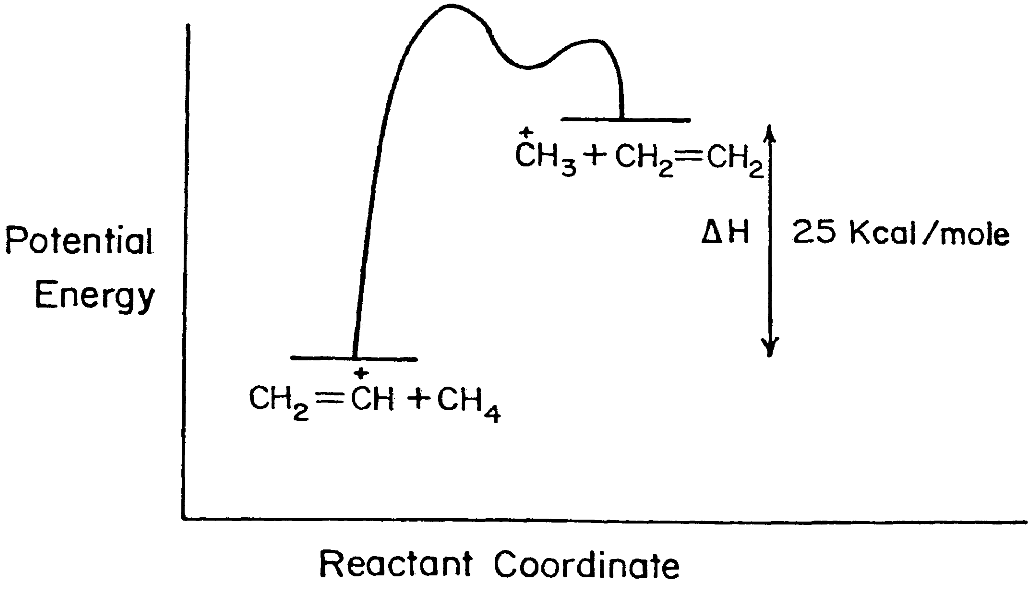
R_1^+; $CH_2{=}\overset{+}{C}H$ R_1H; $CH_2{=}CH_2$

Proton addition to alkynes is also energetically comparable to addition to alkenes. For Figure(2), there is a 5 Kcal/mol stability in favor of the alkyl cation.

$$CH_3\overset{+}{C}H_2 + HC{\equiv}CH \longrightarrow CH_2{=}CH_2 + CH_2{=}\overset{+}{C}H$$

Energy differences of ions tend to be compressed in the liquid phase compared to the gas phase due to solvation effects. Therefore, the differences in stabilities between carbonium ions and vinyl cations in solution are likely to be even smaller [5]. Thus, vinyl cations are not especially unstable. A formulation of an overall energy diagram would include an increase in the activation energy for a vinyl cation intermediate as well as a similar increase in energy for the ground state reactants. The overall difference would then be comparable to similar saturated systems Figure(3).



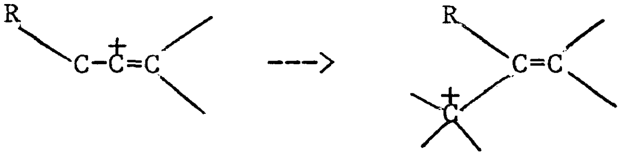


Vinyl cations may then be expected to proceed by an (SN1) mechanism as long as superior leaving groups such as trifluoromethanesulfonate (triflate) are involved. Another criteria is that the vinyl cation intermediate must be stabilized by *α* substituents with electron donating ability or *β* substituents which are capable of positive charge dispersal.

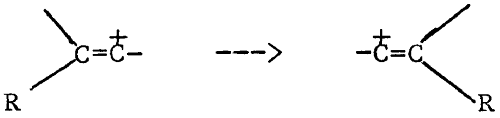
The α-t-Butylvinyl Triflate System; Rearrangements

A characteristic behavior of carbonium ions is their great tendency toward rearrangement. One mode of rearrangement is the alkyl shift where the driving force is generally the formation of a more stable intermediate from a less stable precursor. This may occur with concomitant ion formation and migration, and therefore with anchimeric assistance, or in several distinct stages.

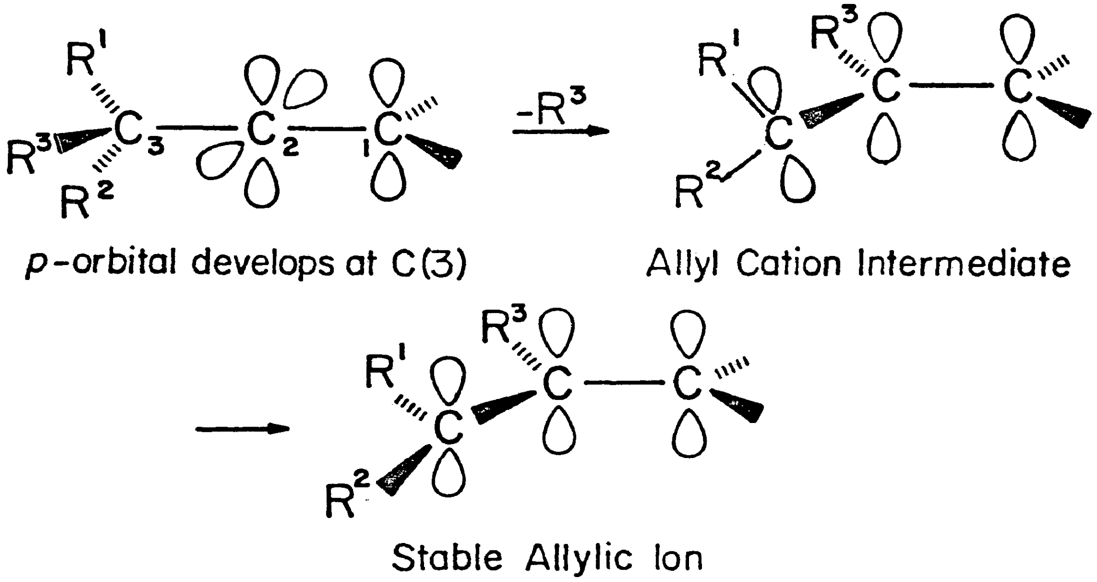
There are two broad categories of vinyl cation rearrangement. The first, migration to the double bond as shown in Figure(4).



Another possible rearrangement is migration across the double bond demonstrated in Figure(5).

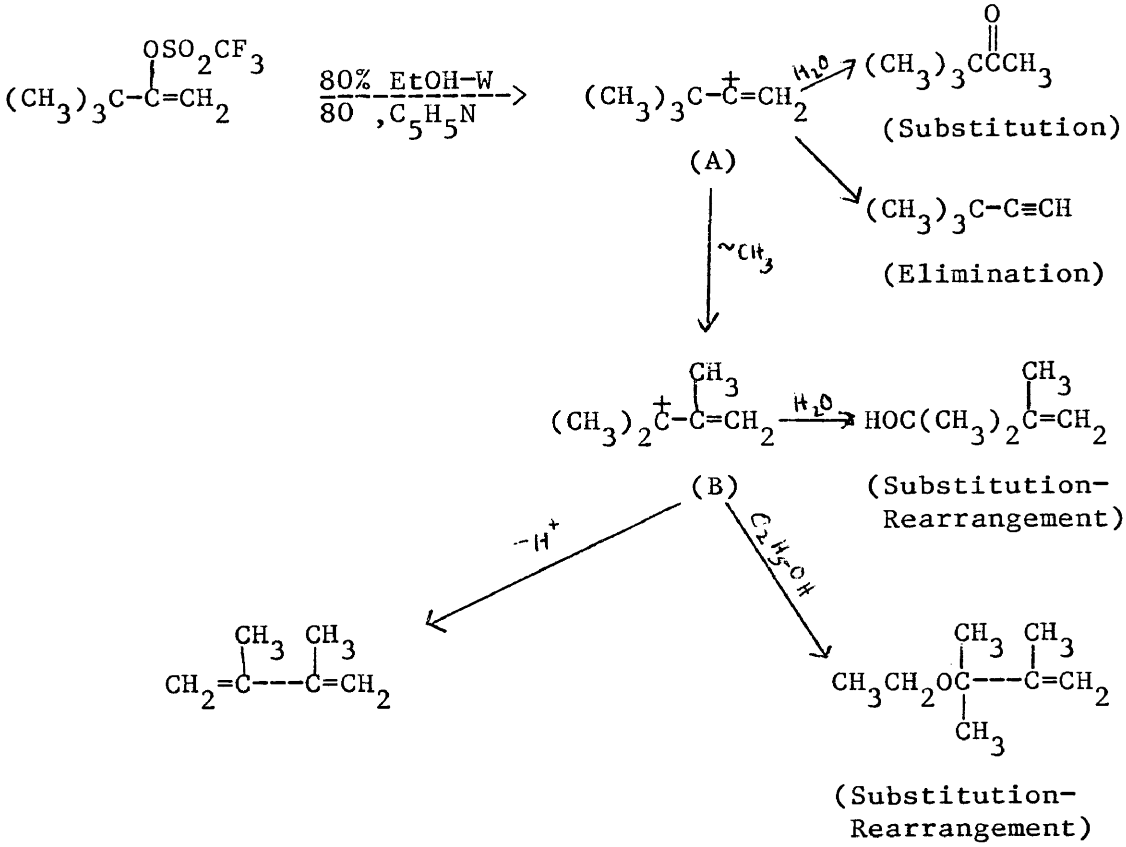


The nature of the migrating group, whether it is a hydrogen, alkyl, aryl, or heteroatom, will greatly effect the ease of rearrangement. Upon initial consideration, one would conclude that migrations to the double bond should result in an allyl cation and therefore readily occur. A more realistic picture Figure(6) indicates that the initially formed intermediate must be a perpendicular allyl cation, which must first undergo rotation about the carbon(2)-carbon(3) bond to give a stable allylic ion [4].



The parent linear allyl cation is 40 Kcal/mole more stable than the perpendicular species [6]. The result has been ascribed primarily to the destabilizing inductive effect of a perpendicular bond Figure(7).

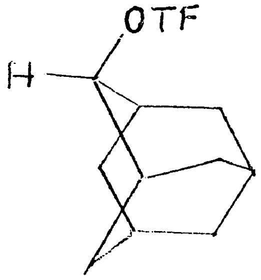
The initially formed intermediate from 1,2 migrations to the double bond are "less" stable than the precursor vinyl cation. Currently, there have been no reports of 1,2 migrations to the double bond in vinyl cations in which the resultant allylic ion is primary (i.e., R(1)=R(2)=H). With alkyl or aryl substituents, additional stabilization may be provided. One example is a vinyl cation generated solvolytically from α-t-butylvinyl triflate [7].



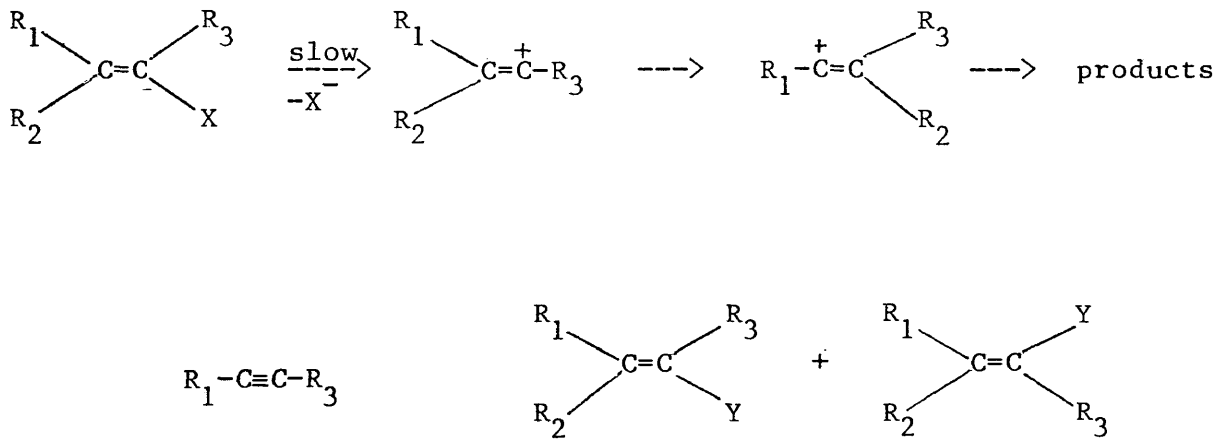
Statistically, 28% of the products were derived from unrearranged ion (A), and 47% of the products from rearranged ion (B). The starting triflate reacts only three times faster than 2-propenyl triflate. There is also a 2:1 rearranged/unrearranged product ratio in 2-propenyl triflate. Therefore, an anchimeric assisted synchronous ionization migration is unlikely. A stepwise process for Figure(8) is more probable.

Discerning a Vinyl Cation Mechanism

Any cationic mechanism of solvolysis exhibits pseudo-first order kinetics. The reaction rate is independent of solvent pH and the concentration of added base. The solvent rate should be dependent on the ionizing power of the solvent. The Winstein-Grunwald m value is usually between 0.5-1.0 ($\log(k/ko)=mY$, where Y is the ionizing power of the solvent). Yet, triflates tend to show lower m-values [53]. In other words, unsaturated triflates show a low response to changing solvent ionizing power. For example, 2-adamantyl triflate Figure(9), gives an m-value of 0.60 as compared to 0.91 for 2-adamantyl tosylate and 1.03 for the bromide ion in aqueous alcohol solvent [53].

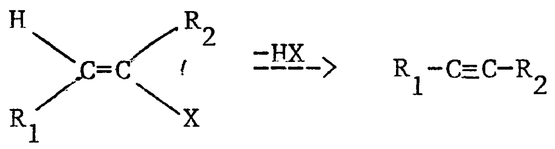


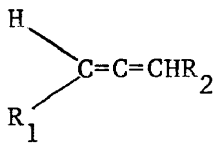
One explanation is the smaller solvent stabilization requirements of the unusually stable trifluoromethanesulfonate ion. Bromide ion being a poorer leaving group than sulfonates should require greater solvent stabilization [53]. In the case of saturated carbonium ions, evidence for the intermediacy of vinyl cations can be deduced from the formation of rearranged solvolysis products. Until further studies have been done (i.e., comprehensive rate studies, secondary deuterium effects and salt effects) rearranged solvolysis products will be the primary argument for α-*t*-butylvinyl triflate proceeding via a vinyl cation intermediate. The triflates are known to be 10^4 - 10^5 times more reactive under solvolytic conditions than the corresponding arenesulfonates [4]. Vinyl triflates should then be favorable precursors [4] for the generation of vinyl cations Figure(10).



In addition to (SN1) heterolysis, there are other mechanisms that can be written to account for the observed products from the solvolyses of the sulfonates. Under neutral or especially basic conditions a synchronous elimination to the leaving group can take place Figure(11).

E2 Elimination Mechanism



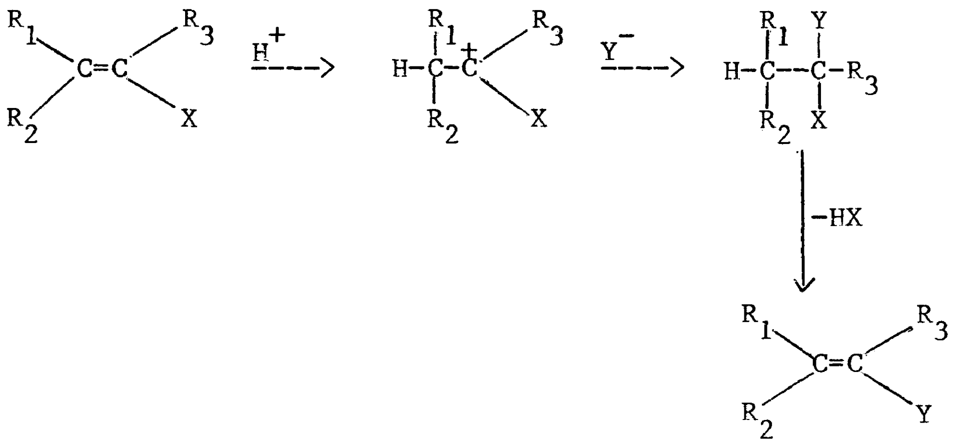


(D)

The corresponding alkyne or allene (D) can be formed. Evidence for the (E2) mechanism is indicated by a considerable increase in the reaction rate when base is added and by a large primary deuterium isotope effect (i.e., trans-2-buten-2-yl triflate k(H)/k(D)=2.01) [4].

The Electrophilic Addition-Elimination mechanism produces similar (SN1) products by an electrophilic attack of a proton on the vinyl substrate. With the formation of a trisubstituted carbenium ion intermediate, it then reacts with the solvent nucleophile leading to the addition product or subsequent elimination of the leaving group HX Figure(12).

Ad_E2 Mechanism

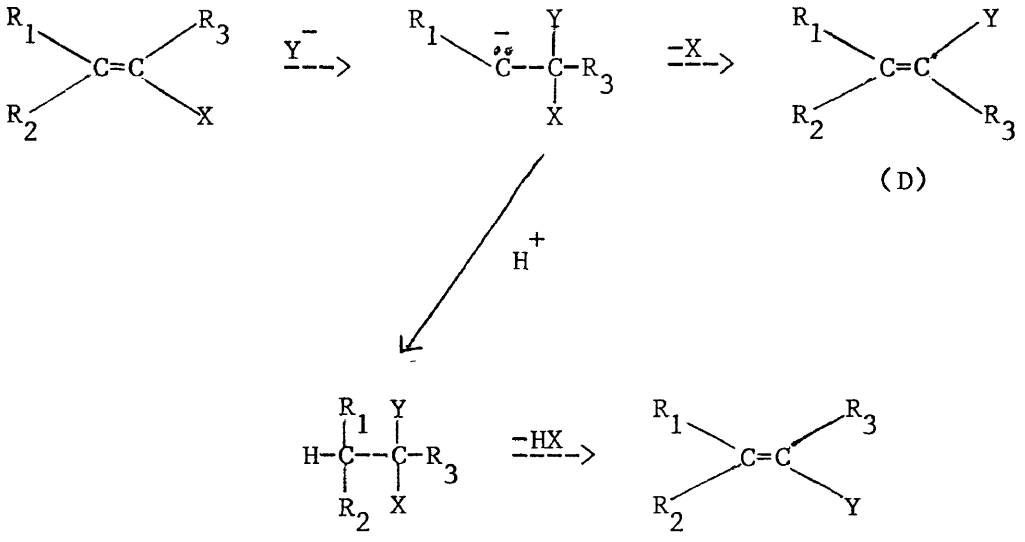


The reaction rate will always be strongly dependent on H+ ion concentration of the solvent medium. When the solvolysis in Figure(12) is carried out in deuterated solvent [4] such as CH_3-COOD or CF_3CH_2OD, contrary to the vinyl cation mechanism,

COOD or CF_3CH_2OD, contrary to the vinyl cation mechanism,

deuterium incorporation into the products is observed, assuming the R groups are hydrogen in the starting substrate. Solvent isotope effects should be present. Special effects of different leaving groups are also evident. With a better electron-attracting leaving group, rate enhancement would be expected for a vinyl cation mechanism. For Electrophilic Addition-Elimination mechanism, a rate retardation results. Finally, there is no evidence of alkyne formation.

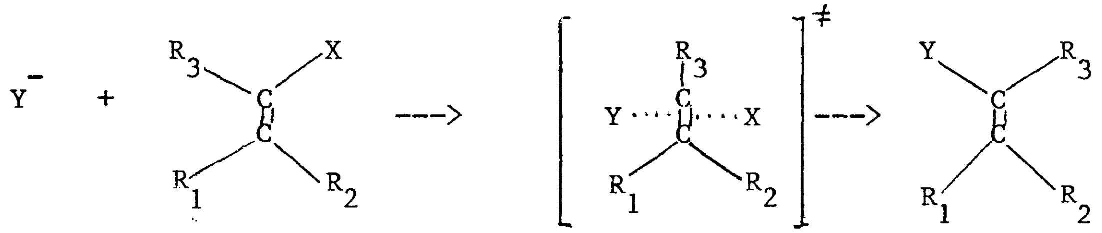
When R(1) or R(2) are equal to hydrogen, the Nucleophilic Addition-Elimination mechanism can take place. The first step consists of an attack by the nucleophilic (Y) on the double bond which after losing (X-), gives E or Z isomers Figure(13).



If strong nucleophiles are present this mechanism may dominate in a second order fashion, where the rate is strongly dependent on the concentration of added nucleophile. One would expect an acceleration of the rate by electron-attracting groups for R(1) and R(2) in the formation of compound(D), where one gets retention of configuration. For example, triarylvinyl arenesulfonates and bromides, $Ar_2C=C(Ar)X$ (X=Br or OSOAr) and *tris*-*p*-methoxyphenylvinyl tosylate, when reaction rates are compared show a sensitivity to the *α*-activating substituent with k(*α*-*p*-MeOCH/k(*α*-ph)=630 [48].

With one step direct (*SN2*) displacement by a nucleophile at the vinylic carbon atom, inversion of configuration of the substitution product in principle should be observed [4]. Such a route has not been observed with the exception of the reaction of *cis*-*β*-halogenostyrenes with nucleophilic bis(dimethylglyoximato)pyridinecobaltate(I) ion. The ease of reaction decreases as the halide on the cis-β-halogenostyrene proceeds from X=I to X=F. This ordering effect in conjunction with the absence of isomerism of either reagent, halogeostyrene or product cis-styrylcobaloxime implies that the displacement of halide ion and the attack of the nucleophile at the β-carbon are sychronous processes, taking place with full retention of configuration [43]. However, no other evidence is yet available to back up the above experiment. For the most part, extended Huckel theory calculations confirm the relative difficulty of (SN2) processes in vinyl systems. This may be due in part to steric arguments, since the approach of a nucleophile may be hindered by R(1),R(2),R(3) substituents from allowing backside displacement to occur Figure(14).

SN2 Displacement Mechanism



Ion Pair Evidence and Scheme

Evidence for the intervention of ion pairs during solvolysis are considered in the classic work of Hughes and Ingold [16] and coworkers in demonstrating common ion rate depression to distinguish between the unimolecular (SN1) and the bimolecular (SN2) mechanisms. The nucleophile is present in large excess compared to the substrate and will therefore cause the appearance of first order kinetics, even for an (SN2) mechanism. With this fact in mind, the kinetic rate data afford no information regarding the appropriate mechanism. Yet, the formation of ions as reaction products might be expected to alter the kinetic behavior during the course of a reaction [16], [17]. Consider Figure(15).

$$RX \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+ + X^- \xrightarrow[H_2O]{k_2} ROH + H^+ + X^-$$

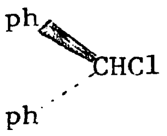
The intermediate carbonium ion R+, may undergo reaction with the solvent giving ROH or with the halide ion regenerating the alkyl halide. By the mass law effect, one may hypothesize that an increase in halide ion concentrations yields a greater return to alkyl halide by k(-1) at the expense of k(2). Table(I) represents a series of experiments in which sovolysis studies of benzhydryl halides Figures(16) and (17) in the presence of common and noncommon ion salts, demonstrating that the rate depressions were not a result of changes in the ionizing power or the solvolysis medium but were a consequence of a common ion effect [18].

Table(I)

Effects of Added Salts on the Initial Rate Constants for Solvolysis of Benzhydryl Halides in 80% Aqueous Acetone at 25° C

	Benzhydryl Chloride	
(.1M) Added Salt	$k(sec^{-1}) \times 10^5$	Change (%)
None	7.00	-
LiBr	8.16	+17
LiCl	6.09	-13

Benzhydryl Bromide	
$k(sec^{-1}) \times 10^3$	Change (%)
1.53	-
1.33	-13
1.94	+27



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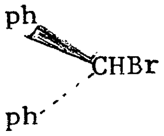


(17)

One would expect similar rate depressions of the four cases in the presence of added salt if the rate depression of the alkyl chloride solvolysis in the presence of chloride ion were a consequence of altering the character of the solvolysis medium by the addition of an ionic species. Clearly, added salt, when the halide was the same as the leaving group, showed depressed rate constants where the presence of a noncommon ion actually led to rate enhancement. The latter effect is a result of an increase in the ionic strength of the solvolysis medium. Since the common ion effect is superimposed upon the ionic strength effect, the common ion effect must be larger than the values in Table(1). The common ion effect is a direct consequence of the recombination of the ionic intermediates formed from ionizing RX. When k, increases upon addition of salt, MX, it is evident that the anions formed by ionization of RX to (R+)(X−) are chemically indistiguishable. Therefore, (R+) and (X−) must be represented as freely dissociated ions with negligible interaction. In conclusion, the common ion effect reaction provides strong evidence for the intermediacy of the "free" ions.

Common ion exchange invariably has been demonstrated using labeled salts, MX*, when the common ion effect is observed [20]. Winstein and coworkers [19] set out to reconfirm the above observation only to find an inconsistency with the proposed free ion Figure(15). Acetolysis of a series of alkyl arenesulfonates were studied and listed in Table(II). All entries are consistent with the free ion scheme showing and expected increase in exchange. The "fly in the ink" is the d,l-threo-3-p-anisyl-1-butyl brosylate. Common ion exchange took place yet there was no evidence of common ion rate depression. Figure(15) ascribes to common ion rate depression and exchange as being both manifestations of the collapse of the dissociated carbonium ion R+ with free halide ion (X-). Winstein and coworkers [19] suggest that certain conditions might not exhibit in solvolytic reactions of the carbonium type, the phenomena of common rate depression and exchange Table(II).

Table(II)

Occurence of Common Ion Rate Depression and Exchange in the Acetolysis of Several Alkyl Arenesulfonates

Arenesulfonates	Common Ion Rate Depression	Exchange
exo-2-norbornyl OBs	No	No
1-p-anisyl-2-propyl OTs	No	-
d,1-threo-3-p-anisyl-2-butyl OBs	No	Yes
d,1-threo-3-p-anisyl-2-butyl OTs	No	-
cholesteryl OBs	Yes	Yes
cholesteryl OTs	Yes	Yes
2-(2,4-Dimethoxyphenyl)-ethyl OBs	Yes	Yes

Ion pair intermediates seemed likely. Consider Winstein's solvolysis in Figure(18) which takes into account the role of ion pairs.

$$\begin{tikzcd}
\mathrm{RX} \arrow[r, shift left, "k_1"] & \mathrm{R^+X^-} \arrow[l, shift left, "k_{-1}"] \arrow[r, shift left, "k_2"] & \mathrm{R^+\ \ X^-} \arrow[l, shift left, "k_{-2}"] \arrow[r, shift left, "k_3"] & \mathrm{R^+ + X^-} \arrow[l, shift left, "k_{-3}"] \\
\mathrm{I} & \mathrm{II} \arrow[d, "\mathrm{SOH}"', "k_s^{II}"] & \mathrm{III} \arrow[d, "\mathrm{SOH}"', "k_s^{III}"] & \mathrm{IV} \arrow[d, "\mathrm{SOH}"', "k_s^{IV}"] \\
 & \mathrm{ROS} & \mathrm{ROS} & \mathrm{ROS}
\end{tikzcd}$$

The ionization of an alkyl halide or arenesulfonate (I) proceeds through a series of more dissociated ion pair intermediates, where (II) is the intimate, internal, or "tight" ion pair. (III) is the "solvent-separated" or external ion pair, and (IV) is the "freely dissociated" carbonium ion. Winstein defined several terms regarding reverse reactions which regenerate covalent RX under the general classification of return [20].

1. Internal Return - collapsed of intimate (or internal) ion pair (II-I).
2. External ion pair return - combination of dissociated carbonium ion R+ and X- (III).
3. External ion return - a broader category which includes both 1 and 2 above.

4. External return - a broader category which includes both 2 and 3 above.

Attack by the solvent may take place at any of the three types of ions. The intermediate involved is governed by the nature of RX, on the solvent choice, and perhaps leaving group choice. As R+ increases in stability, the site of the solvent attack would shift to a more ionized intermediate [19]. The d,l-threo-3-anisyl-2-butyl brosylate substrate gives a less stable carbonium ion relative to the following compounds. Therefore, dissociated carbonium ions would not be formed under the conditions of acetolysis, and one would predict that solvent attack would take place only at the solvent-separated stage (III).

Due to the close association of the anion in the intimate ion pair (II), one would expect effective blocking of solvent attack from that particular side. Consequently, a largely inverted configuration would be expected [21]. Derivatives solvolyzing via anchimerically assisted ionization would be expected to react only at the stages of solvent-separated ion pair (III) and dissociated carbonium ion (IV) [22]. The classic example is the bridged "nonclassical" ion, where the backside of the intimate ion pair would be shielded against solvent, and solvent attack on (II) would be unimportant.

Winstein's results provide strong support for the intervention of ion pairs as intermediates in acetolysis reactions. Anion exchange can occur at the solvent-separated ion pair (III) or the dissociated carbonium ion (IV) stage but not at the intermediate ion pair stage.

The common ion rate depression and exchange provide a useful tool in further understanding the nature of the intermediates in solvolysis reactions. In the case of the free cation (IV), both the mass law effect and exchange result in the absence of common ion rate depression. Yet, exchange continues, capture of the solvent may occur at the ion separated pair (III) leaving the importance of ion (IV) negligible. It is vital to be certain that anion exchange does not occur by way of a direct displacement.

Common ion exchange would also be observed even though a free or solvent-separated ion is not formed. Winstein, Ledwith, and Hojo [23], demonstrated that radiochloride exchange of p-chlorobenzhydryl chloride in anhydrous acetone separated ion is not formed. Winstein, Ledwith, and Hojo [23], demonstrated that radiochloride exchange of p-chlorobenzhydryl chloride in anhydrous acetone takes place predominantly by (SN2) attack on the intimate ion pair. When the substrate has a propensity for a carbonium ion mechanism (m value > 0.5), and the solvent has high degree of ionizing power, direct displacement should be minimized [24],[11].

Winstein, Clippinger, Fainberg, and Robinson [25], reported that several alkyl arenesulfonates exhibit highly unusual salt effects. In the presence of varying amounts of lithium perchlorate (a weak nucleophile), the titrimetric rate constants were greatly increased in the presence of small amounts of $LiClO_4$. However, when the $LiClO_4$ was increased, the rate enhancement leveled off and the normal salt effects were observed. Since the special salt effect eliminated only a certain portion of the ion pair return (at low concentrations), the data suggests that return comes about from two different intermediates. Strong supporting evidence in favor of the special salt effects being a consequence of preventing a certain portion of ion pair return is available from studies of salt effects on rate constant for ionization [21].

Winstein and his coworkers [25] propose that the special salt effect is a consequence of interference with return from solvent-separated ion pairs. For substrates that undergo return from intimate ion pairs, normal salt effects are observed. In the case of internal return and external ion pair return, the addition of $LiClO_4$ interferes with external ion pair return causing an increase in the titrimetric rate constant excluding any influence on the ionization rate constant other than the normal salt effect. Beyond a certain concentration of added salt, return from the solvent-separated ion pair is negligible due to the concentrations of ion pair being small relative to salt and therefore, the normal salt effect is the only observable characteristic mechanism.

Previously it was argued that in anionic exchange, such exchange may occur at the solvent-separated ion pair or the free carbonium ion stage but no attack of the intimate ion pair. A correlation should exist between the anion exchange and the special salt effect. Consider Table(III) which portrays an exact correspondence between the anion exchange and special salt effect [20].

Table(III)

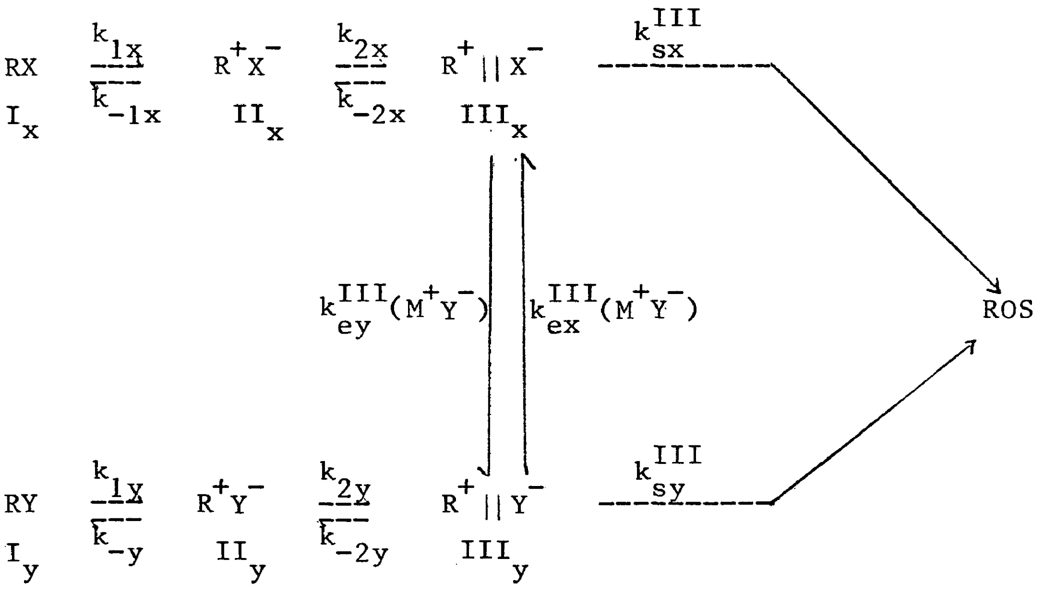
Correspondence of the Special Salt Effect and Anion Exchange in Acetolysis

Compound	Exchange	Special Salt Effects (LiCl)
2-exo-norbornyl OBs	no	no
threo-3-p-anisyl-2-butyl OBs	yes	yes
cholesteryl OTs	yes	yes
2-(2,4-Dimethoxyphenyl)-ethyl OBs	yes	yes
p-chlorobenzhydryl chloride	yes	*
1-p-anisyl-2-propyl OTs	yes	yes
cholesteryl OBs	yes	yes

* Only two concentrations of added salt were studied; extrapolation gives a ratio of 1.06 for k_{ext}/k_t

Elimination of external return appears to be associated with the special salt effect, and salts such as $LiClO_4$ act as efficient traps for the solvent- separated ion pair. A proposed Figure(19) represents the special salt effect as a consequence of an exchange process taking place at the solvent-separated ion pair stage.

Below is a possible mechanism for the special salt effect omitting the dissociated carbonium ion (IV) for simplicity Figure(19).



Experimental evidence [21] shows that a variety of salts can produce a special salt effect (i.e., KOAc, $HClO_4$). Yet, the common ion salt is only capable of a normal salt effect on the ionization rate but is unable to exercise a special salt effect. This key piece of information provides strong evidence for a mechanism of the special salt effect which involves a specific interaction between a solvolytically generated ion pair (III) and the ions of the added salt MY.

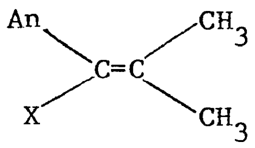
Consider a closer examination of the specific reaction that results in a special salt effect Figure(20).

$$R^{+}||X^{-} \quad + \quad (M^{+}Y^{-}) \quad \underset{k_{ey}^{III}}{\overset{k_{ex}^{III}}{\rightleftharpoons}} \quad R^{+}||Y^{-} \quad + \quad (M^{+}Y^{-})$$

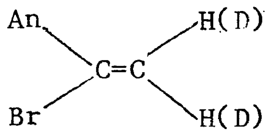
The equilibrium above should be subject to a common ion effect. For a compound which ordinarily does not show a common ion effect, upon addition of a noncommon salt, the overall exchange reaction above is inhibited. As a result no special salt effect is apparent. Such inhibitions of the special salt effect are categorized as "induced" common ion rate depressions [26]. In summation, one may obtain valuable information about the rate constants for the formation of the solvent-separated ion pairs using anion exchange and special salt effects.

Applications of Ion Pairs in Aryl Vinyl Systems

Work done by Rappoport and coworkers confirm that the aryl vinyl systems solvolyze mainly by an (SN1) mechanism via intermediate ion pairs. In considering the system 1-(4-methoxyphenyl)-2-methylprop-1-enyl halide Figure(21) the leaving group ratios fit an (SN1) reaction mechanism, and the appearance of strong common ion rate depression when X=Cl or Br.



(21)

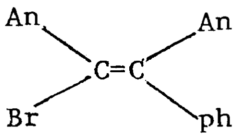


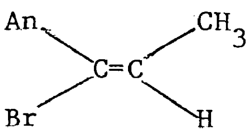
(22)

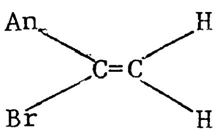
More than 92% of the solvolysis products arise from dissociated cations for X=Br in TFE (trifluoroethanol) solvent [13]. Yet, for α-bromo-4-methoxystyrene Figure(22) no evidence of common ion rate depression in 50% (v/v) of EtOH/W or acetic acid solvents.

Isomerization of unreacted starting material was not observed in EtOH/W solvent but was found in acetic acid solvent. The information was rationalized by a rate determining formation of a tight ion pair with rapid solvent capture of EtOH/W but slow solvation in the acetic acid solvent allowing time for isomerization of the starting material by internal return.

The importance of the β-substituents may help explain the observation of ion pair return in Figure(21) but not in Figure(22). Rappoport proceeded to study the amount of ion pair return in 80% (v/v) EtOH/W in the following molecules Figure(23).







The amount of ion pair return decreases with the decreasing size of the β-substituents. Aryl vinyl deviations RX frequently show strong common ion rate depression by anion (X-) [13]. This phenomenon was observed for Figures (21) substituents. Aryl vinyl deviations RX frequently show strong common ion rate depression by the anion (X-) [13]. This phenomenon was observed for Figures (21) and (22) in TFE and aqueous TFE. Since a limit to the rate depression was not achieved greater than or equal to 92% of the solvolysis products in TFE, a large fraction of them in aqueous TFE, are formed from "dissociated" vinyl cations [13].

An explanation [14] for the observation concludes that the bulky β- substituents shield the exposed cationic orbitals from the solvent. There is an increase in the lifetime and selectivity of the vinyl cation which leads to an increase of ion pair return. The large bulky groups may be expected to decrease the amount of nucleophilic involvement in solvolysis and decrease the observed Winstein-Grunwald "m" values [15].

Secondary Deuterium Isotope Effects

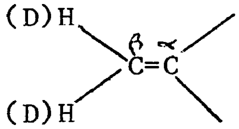
Another method for the detection of ion pairs is the secondary deuterium isotope effect. Carbon-deuterium bonds have a lower zero point vibrational energy due to the heavier mass of deuterium as compared to carbon-hydrogen bonds. A great advantage of measuring rates of deuterated and non-deuterated compounds is that those compounds behave the same chemically save for their differences in kinetic behavior.

For primary isotope effects, the C-H or C-D bond is broken during the transition state of the reaction. Since a vibrational mode is destroyed in the transition state, the energy levels of both bonds are no longer important. Therefore, the activated complex in the transition state is the same energy level for the C-H or C-D bond. With a lower zero point energy for the C-D bond, a greater activation energy is expected and thus a slower reaction rate for the saturated molecule. The maximum effect occurs when the hydrogen being transferred is bound about equally to two other atoms in the transition state.

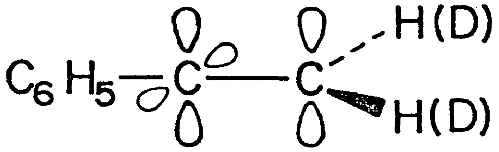
At room temperature, the calculated maximum for the isotope effect involving C-H bonds is about 7. This value decreases at higher temperatures [27] and bond breaking is more or less than half complete in the transition state.

Primary isotope effects provide some indication as to where the transition state lies relative to reactants and products, as well as whether or not the substituted hydrogen atom is broken in the transition state. Usually, k(H)/k(D) will be less than or equal to 2.

The secondary isotope effects are dependent on changes in the vibrational force constant of the C-H or C-D bond in going from the ground to transition states. The temperature, leaving group, solvent, and modifications in the substrate structure all can modify the magnitude of the α-secondary deuterium isotope effects Figure(24).

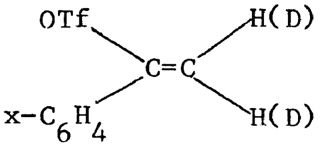


β-deuterium dependencies are similar to α-deuterium except for the importance of the leaving groups [59]. The β-deuterium isotope effects in solvolytic reactions have been ascribed to differential hyperconjugative overlap of the C-H(D) bond with the developing vacant p-orbital at the reaction site [28]. Consider Figure(25) below [12].



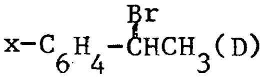
The hyperconjugative interactions with the carbonium ion site result in changes of the vibrational force constants via a partial charge dispersion at the cationic center. This causes an isotope effect due to the weakening of a C-H(D) bond.

The effect of substituents upon the isotope effect is revealing. Highly destabilizing substituents such as p-NO_2 or p-CF_3, result in an increased β-isotope effect indicating a greater need for hyperconjugative stabilization of the developing empty p-orbital with increasing electron isotope effect indicating a greater need for hyperconjugative stabilization of the developing empty p-orbital with increasing electron withdrawal by the substituents [28]. Consider Figure(26).



x; p-NO_2, p-CF_3

This trend was also observed in the saturated substrate [29] but of a greater magnitude Figure(28).

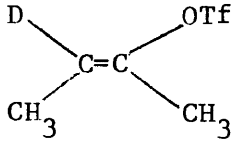
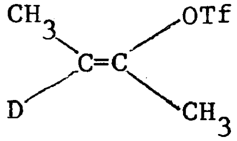


$$x\text{-}C_6H_4\text{-}\overset{Br}{C}HCH_3(D)$$

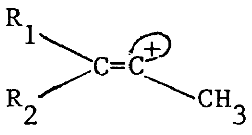
The dihedral angle between the empty p-orbital and the b-C-H bond plays a strong role in the *β*-isotope effect. Such strong dependence provides a maximum effect when the dihedral angle is 0° and an inverse effect at 90° [30]. The vinyl cation with its linear geometry satisfies this requirement, and one observes large *β*-deuterium effects in the para substituted *α*-styryl triflates [28] (k(H)/k(D)=1.74 for the p-Cl; k(H)/k(D)=1.45 for parent compound; all done in 80% (v/v) EtOH/W at 75°) as compared to those observed [29] in the solvolysis of 1-aryl-1-halogenothanes where k(H)/k(D) effects range from 1.113 for the p-methoxy isomer to 1.224 for the parent compound.

The importance of a *trans* periplanar arrangement is considered [4] in the following Table(IV).

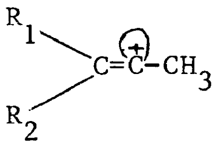
Table(IV)

	Substrate	Solvent(Temp°C)	k_H/k_D
cis-2-buten-2-yl triflate		60% EtOH-W(75°)	1.25
trans-2-buten-2-yl triflate		60% EtOH-W(75°)	2.01

The *trans* substrate deuterium effect is 4 times ($\Delta\Delta G\#$ = 62 kcal/mol) larger than the *cis*. Moreover, the relative kinetic rate at 75° in 60% EtOH/W is 2.26 x 10 exp(-3) sec(-1) for the *trans* and 8.13 x 10 exp(-5) sec(-1) for the *cis* adduct. With such a discrepancy in kinetic rates, it would appear that the two compounds proceed by different solvolysis mechanisms. The dependence on sterochemistry may be due to a bent sp2-hybridized transition state where the developing electron deficient p-orbital interacts more effectively Figure(28) as compared to a linear sp-hybridized transition [33] state Figure(29).



(28)



(29)

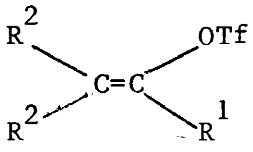
The trans adduct possess a proper configuration for an elimination mechanism where bond breaking occurs in the transition state. The k(H)/k(D) may be characterized as a primary isotope effect. The cis, may proceed by a unimolecular ionization and a vinyl cation intermediate [31].

Consider the product isotope effects presented in Table(V) [33].

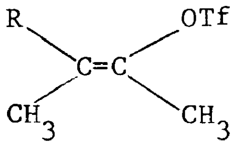
Table(V)

Deuterium Isotope Effects for Triflates in 60% EtOH-W at 75°

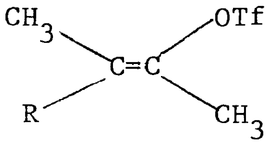
	Kinetic Effect	Product Effect
Compound	k_H/k_D	k_H/k_D
2b	1.54	1.95
2c	.86(25°C)	-
2c	.96(75°C)	1.07
2c	1.01(120°C)	-
3b	1.25	1.26
4b	2.01	-



(2)



(3)



(4)

*Kinetic effect: The ratio for the protio- and deuterio- compound give direct measure of the kinetic deuterium isotope effect. Similarly, the ratio of allene to ketone for the protio-compound over the same ratio for the deuterio-compound serves as a measure of the deuterium isotope effect in product formation (i.e., the product isotope effect).

(2)	(3)	(4)
b; $R^1 = CD_3$, $R^2 = CH_3$	b; R = D	b; R = D
c; $R^1 = CH_3$, $R^2 = CD_3$		

There is a close parallel between the product and the kinetic deuterium isotope effects in substrate. The product isotope effects in (2b) and (3b) involve breaking the isotopically substituted C-H(D) bond in the transition state. Therefore, one would expect primary isotope effects ranging in value from 3 to 9. The low magnitude of the experimentally observed product isotope effect must mean that the transition state for product formation occurs early along the reaction pathway and must resemble the reactant (i.e., intermediate vinyl cation). This in turn implies that the elimination of a β-proton from a vinyl cation and formation of either allene or alkyne must be a low energy process with a very small activation energy. This is not unreasonable since β-elimination must compete favorably with solvent collapse of the intermediate ion which is undoubtedly a low energy process [32].

In summary, β-secondary deuterium isotope effects in vinylic solvolyses are considerably larger than in analogous saturated systems. Perhaps owing to the greater need for hyperconjugation stabilization in the unsaturated system and a larger bond overlap across the shorter double bonds of the vinyl system [4]. The β-deuterium isotope effects in vinyl cations, analogous to saturated carbonium ions, are hyperconjugative in origin and are even more strongly dependent upon the dihedral angle between the b-C-H bond and the developing empty p-orbital than in carbonium ion systems. And lastly, the product isotope effects [32] indicate that the β-elimination of a proton from an intermediate vinyl cation proceeds easily with a very small activation energy.

Applications on a "Cautious" Note

Since the magnitude of the secondary deuterium isotope effect is highly indicative of the mechanism, Shiner has found it prudent to discuss secondary isotope effects in the context of Winstein's ion pair scheme Figure(18). Consider Table(VI).

Table(VI)

Some Illustrative α-Deuterium Isotope Effects in Solvolysis Reactions

Substrate	Solvent(%)	Mechanistic Assignment	k_H/k_D
2-adamantyl tosylate	70,97T; 50E	k_2	1.23
3-pentyn-2-yl tosylate	70T	k_2	1.26
3-pentyn-2-yl bromide	70T	k_2	1.123
3-pentyn-2-yl iodide	70T	k_2	1.089
1-phenylethyl chloride	50,80E	k_2	1.15
5,5,5-trifluoro-3-pentyn-2-yl OBs	50E	k_s^I	1.050
2-propyl OBs	TFA	k_2	1.22
	97T	k_s^{II}	1.152
	50T	k_1	1.122
	90F	k_s^I, k_1	1.083
3,3-dimethyl-2-butyl OBs	70,97T	k_1	1.15
benzyl OBs	97T,95E	-	1.175,1.053
ethyl tosylate	W	k_s^I	1.020
methyl tosylate	W	k_s^I	0.984

Maximum α-deuterium isotope effects are observed when k(2) is rate limiting. If k(3) were rate limiting, higher value of k(H)/k(D) would be expected. So far, only the equilibrium α-deuterium isotope effect of 1.29 has been observed [35]. One observes lower values, about three-quarters of the maximum observed value when nucleophilic attack occurs at the free ion state, the solvent-separated ion pair or the intimate ion pair. When nucleophilic attack occurs at the covalent substrate, k(IS), classical (SN2) mechanism is suggested.

In the last two entries, one does see a slight deviation from the expected k(H)/k(D)=1. This may in fact be due to the leaving group and on the structure (i.e., methyl vs ethyl).

There are limitations to Shiner's secondary deuterium isotope interpretations as seen in Table(VI). Shiner brings to light this complication: "Thus, one of the classical examples of borderline solvolyses seems to be borderline in a bewildering number of ways! As many as four different steps, k(1),k(2),k(IS),k(IIS) can be made the dominant rate-controlling influence depending on the choice of solvent. It is not surprising that because of this variety, it is difficult to find conditions which effectively isolate one mechanism to the exclusion of others. Rather, the change appears to be much more continuous with a mixture of mechanisms being the rule rather than the exception." [36]. In the absence of other evidence, there can be no definitive mechanistic conclusions for (1.22 > k(H)/k(D) > 1.0) sulfonates concerning involvement of the solvent nucleophile or ion pairing phenomena since they both conceivably could be involved. A further complication is the distinguishability between the solvent nucleophile's involvement in the intimate k(1) ion pair or the solvent-separated ion pair. Recent mathematical analysis of isotope effects result in a model of the ion pairs with a rearside partially bound to the solvent [37]. The only concluding statement in light of the previous results is that nucleophilic solvent assistance appears to be involved in the rate determining step if an observed α-deuterium solvolysis isotope effect is significantly less that three-quarters of the maximum value for a given leaving group. In other words, in the absence of other evidence, the observation of an α-deuterium isotope effect of intermediate magnitude ($1.22 > k(H)/k(D) > 1.03$ for sulfonates) does not proVide definitive mechanistic information since either nucleophilic solvent involvement or ion pairing phenomena or both may be responsible.

Cyclopentyl p-Bromobenzenesulfonate

As was discussed previously, relying solely on secondary deuterium isotope effects to explain mechanistic "headaches" in solvolysis can be misleading. Therefore, product studies and salt effects in conjunction with isotope effects help "unwind" the intricacies of the solvolytic pathway of a particular compound.

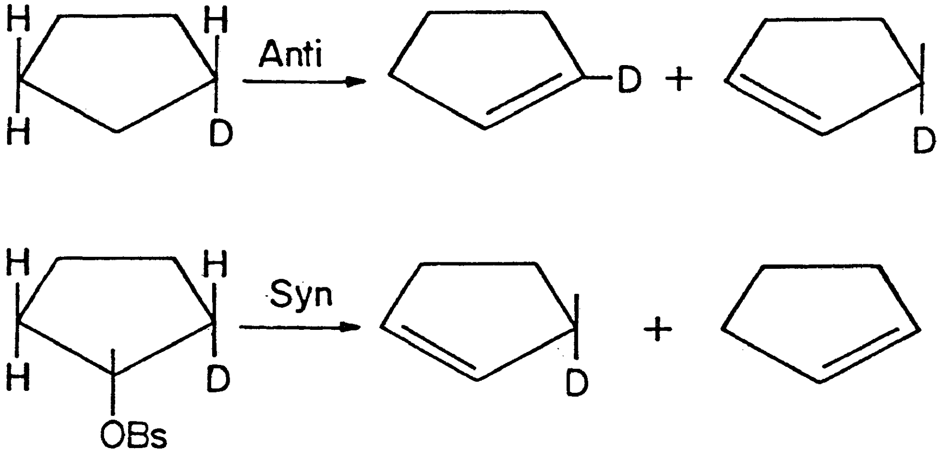
Shiner's work with cyclopentyl p-bromobenzenesulfonate demonstrates this utility for a saturated system.

Deuterium isotope effects on the rates of solvolysis and stereochemical results of substitution have provided evidence that the solvolysis in ethanol- water solvent involves a rate determining substitution and elimination of the reversibly formed intimate ion pair. While in TFE, elimination and substitution proceeded from the solvent-separated ion pair after its rate-determining formation to the tight ion pairs. Evidence establishing the mechanism in EtOH/Water solvents are moderate α- and β-deuterium isotope effects, (k(H)/k(D)=1.14-1.15), and 95% inversion of configuration of the reaction center in cyclopentanol and cyclopentylethyl ether products. If the substitution products were derived mainly from the solvent-separated ion pairs, then a decrease in the solvent ionizing power would decrease the relative amounts of the substitution product since the competitive elimination occurs at an earlier stage of the reaction. Comparison of products formed in 70% and 100% EtOH/Water prove that this is not the case Table(VII).

Table(VII)

Vol. (%) Ethanol		All H(mole%)
(70)	Alkene	21.9
	Alcohol	45.6
	Ether	32.5
(100)	Alkene	11.8
	Alcohol	-
	Ether	88.2

If the substitution products are derived mainly from the tight ion pair, then an increase in the basicity and a decrease in polarity by adding ethanol should favor elimination. This is experimentally observed [39]. Consider the diagram below in Figure(30).

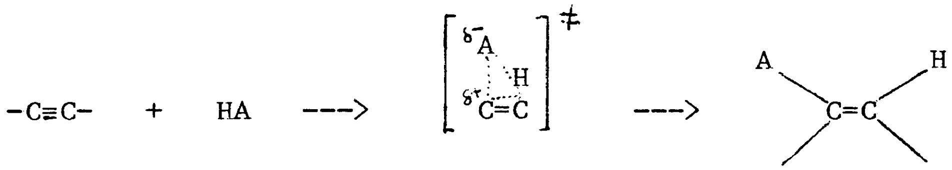


Elimination is mostly *anti* in EtOH/Water solvents. The isotope effect on the *product ratio* (re is the rate of elimination; rs is the rate of substitution) is 1.05 for *cis-β*-deuterium and 1.17 for the *trans*- *β*-deuterium. This information might be explained for the tight ion pair where the leaving group is still in the vicinity of the carbonium ion and therefore hinders solvent attack from the *cis* side.

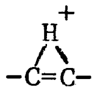
In TFE/Water solvents, the stereoselectivity in the elimination with respect to the position of the *β*-hydrogen is strongly diminished in comparison with the solvolysis in EtOH/Water solvents. The isotope effects for the product ratio in TFE/W for *cis-β*-deuterium and *trans-β*-deuterium were 1.22 and 1.29 respectively (reported in Shiner's earlier work) [41]. However, in later work [40] TFE/Water solvolysis results indicate that *syn* elimination is favored over *anti* by a factor of 4. This implies that elimination by a nonbasic solvent is sufficiently slow so that it is dominated at the ion pair stage by internal elimination of the *β*- hydrogen by the leaving group [40]. One must now consider that in the weakly nucleophilic TFE/Water solvent, there is a competition between *syn* elimination and a rate determining formation of the solvent-separated ion pair. Further support for the above proposal comes from solvolysis of cyclopentyl *p*-bromobenzenesulfonate in aqueous hexafluoroisopropyl alcohol solvent. HFIP is a weaker nucleophile than TFE, and experimental results demonstrate that with the decrease in polarity, conversion to the solvent-separated ion pair becomes negligible, and *syn* elimination by the leaving group predominates.

Electrophilic Addition to Alkynes

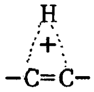
Electrophilic additions to olefinic systems [44] have received considerable attention. The analogous additions to acetylenic systems have received somewhat less attention. There are three mechanisms that must be considered for the addition of an acid (HA) to an acetylene (Y). Consider first a synchronous attachment of (HA) across the acetylenic bond with *syn* stereospecificity Figure(31).



The Ad(E)2 (addition, electrophilic bimolecular) [16] discussed earlier, involves a stepwise addition via a carbonium ion intermediate. For this bimolecular scheme, two considerations concerning the intermediate structure must be realized. If the intermediate cation has a bridged structure, anti addition should occur where the backside attack is analogous to the (SN2) mechanism as in Figure(32) and (33).

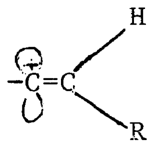


(32)



(33)

For an open vinyl cation, stereospecific addition would not be expected. Thus, syn and anti products would be expected. The linear cation, however, has the developing vacant p-orbital lying in the plane of the molecule. Consequently, there is a sensitivity to steric and electronic characterization of the groups bonded to the β-carbon atom. Results [45],[46] confirm this steroselectivity of the linear vinyl cation Figure(34).



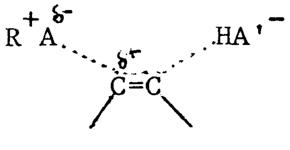
Open Vinyl Cation

The final scheme includes a transition state in which both the C-H and C-A bonds are formed in the transition state. Yet, H+ and A- are derived from two different molecular ionic species. This termolecular mechanism is classified as Ad(E)3 Figure(35).

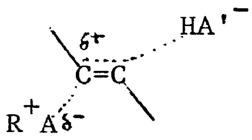
$$Y + RA + HA' \longrightarrow [R^{+}A \quad Y \quad HA']^{\ddagger} \longrightarrow$$

$$YHA + R^{+} + A'^{-}$$

In principle, Ad(E)3 addition should be able to occur syn Figure(36) or anti Figure(37). Anti addition is preferentially observed over syn [47].



(36)



(37)

3-Hexyne added to HCl gave almost exclusively anti in acetic acid [47].

There are several factors which affect the balance between the Ad(E)2 and Ad(E)3 addition mechanism. In the case of the hydrochlorination of 3-hexyne, observations of an Ad(E)3 mechanism have been reported [47]. Upon increase in reaction temperature, the Ad(E)2 mechanism is favored relative to Ad(E)3 addition. In the presence of substituents at the acetylenic bond which can delocalize a positive charge, an Ad(E)2 mechanism appears to be more favorable. Such is the case for the 1-phenyl propyne system which follows an Ad(E)2 mechanism and reacts via a tight ion pair leading to predominant syn addition [58]. For the Ad(E)3 scheme, a simultaneous presence of an effective nucleophile as well as a strong acid are essential.

Clear evidence may be found upon comparing the ratio, products, and stereochemistry of the addition of 3-hexyne and 1-phenylpropyne. Results show that they react at comparable rates. The presence of tetramethylammonium chloride (TMAC) or water produce a remarkable acceleration in rate Table(VIII).

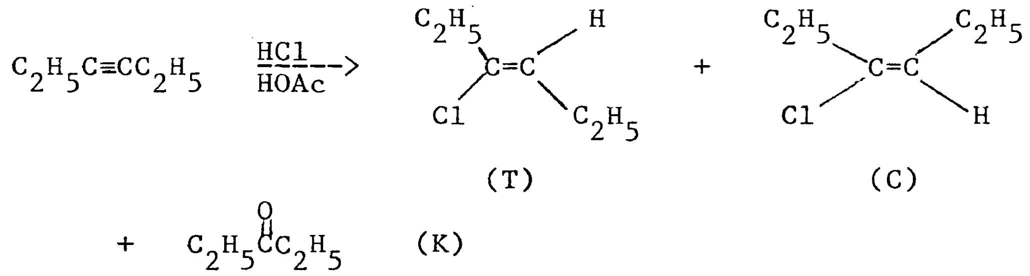
Table(VIII)

M [HCl]	M [C_6H_{10}]	M(sec^{-1}) 10^7 x R	M [TMAC]
.60	.81	.92	-
.60	.81	3.1	.054
.60	.81	6.1	.107
.60	.81	20.0	.427

If an Ad(E)3 mechanism is important in which one molecule of HCl serves as an electrophile and another as a nucleophile, then the reaction leading to dichloride should be accelerated by chloride salts since these would serve as more effective souces of nucleophilic chloride than would HCl. This is observed in Table(IX). Also observed, is a switch over to Ad(E)2 from Ad(E)3 for 3-hexyne in acetic acid as you increase the temperature Table(IX).

Table(IX)

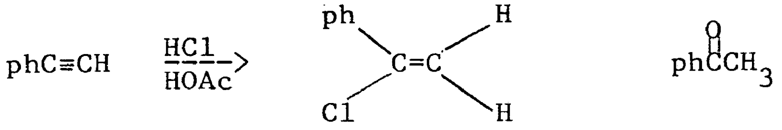
Temp(°C)	M [HCl]	M $[C_6H_{10}]$	$M(sec^{-1})$ 10^7 x R	T	C	K
25	.23	.81	.061	32±1	1.4±.2	66±1
50	.23	.81	.92	25±2	2.5±.4	72±2
80	.23	.81	12.5	25±1	5.2±.2	70±1



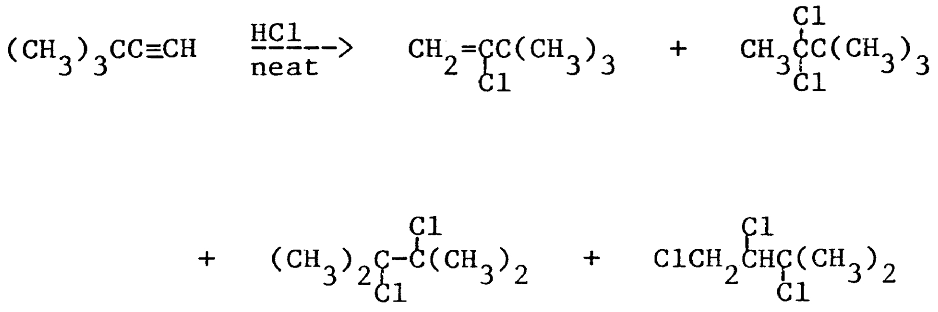
For the addition of phenylacetylene, results show the reaction to proceed exclusively via Ad(E)2 mechanism. The greater ratio of chloride to ketone, 12:1, is consistent with that expected from a collapse of a carbonium-chloride ion pair. Also, the fact that a 0.2M chloride salt increases the reaction rate by a factor of only 2 and does not increase the fraction of chloride formed implicates an Ad(E)2 process [52]. In fact, the presence of 0.2M chloride salt actually results in a decrease in the ratio of chloride to ketone (7:1) Table(X).

Table(X)

Acetylene	M [TMAC]	M(sec^{-1}) [10^7 x R]	Chloride	Ketone
phC≡CH	0	79	92	8
	0.2	174	88	12



In the presence of acetic acid solvent, the reaction occurs via a competing Ad(E)3 addition of HCl and acetic acid. With elimination of the solvent media, substantial amounts of products (30-60%) were formed from methyl migration. Such results are consistent with an Ad(E)2 mechanism inVolving a vinyl cation intermediate [49] Figure(38).



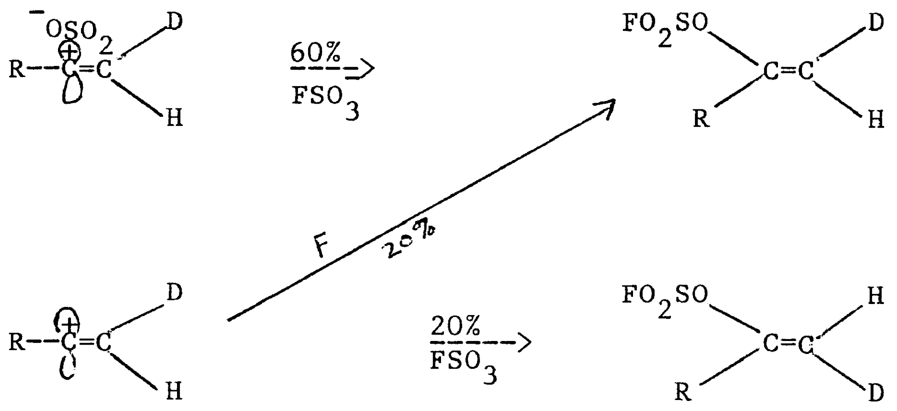
$$(CH_3)_3CC\equiv CH \xrightarrow[\text{neat}]{HCl} CH_2{=}\underset{Cl}{C}C(CH_3)_3 + CH_3\overset{Cl}{\underset{Cl}{C}}C(CH_3)_3$$

$$+ (CH_3)_2\underset{Cl}{C}{-}\overset{Cl}{C}(CH_3)_2 + ClCH_2\overset{Cl}{C}H\underset{Cl}{C}(CH_3)_2$$

By choosing appropriate reaction conditions, involvement of the Ad(E)3 mechanism may be minimized. Olah and Spear [49] reported a study involving a series of alkynes with fluorosufuric acid (FSO_3H highly acidic and weakly nucleophilic).

The formation of distinct ionic intermediates should be strongly favored over the Ad(E)3 scheme under such conditions. The following Figure(39) is a suggested mechanism involving a vinyl cation-fluorosulfate (FSO_3^-) ion pair intermediate and a free vinyl cation intermediate.

$R{-}C{\equiv}CH + DSO_3F$



"<u>Free</u>" Vinyl
Cation

The scheme suggests an initial protonation of the terminal alkyne to form an open vinyl cation-(FSO_3^-) ion pair which subsequently collapes to the <u>syn</u> product 60% of the time. The other 40% of the vinyl cations escape the solvent cage to form the "free" open vinyl cation which reacts in a non-stereospecific manner by nucleophilic attack forming a statistical _syn_ and _anti_ addition [49]. One cannot rule out the possibility that 20% _anti_ addition observed is caused by external attack on the initiallly formed ion pair. It was found that the 80:20 ratio for the _syn_ and _anti_ adducts did not change over an extended period of time, thus ruling out any acid-catalyzed isomerization by excess acid. Thus, free, open vinyl cations with equivalent groups at the β-carbon will give statistical _syn_ and _anti_ addition (i.e., 50/50).

This paper will focus on solvolysis studies of α-_t_-butylvinyl triflate. Such work is an important piece in the overall scheme of vinyl cation mechanisms. Work is currently in progress on the addition of 2-Butyne and triflic acid producing and alkyl vinyl triflate system. The alkyl substituent in the vinyl cation unlike α-_t_-butylvinyl triflate is nonrearranging. Product studies as well as kinetic studies for the arylvinyl bromide system (1-bromo-1-mesitylethene) are also under current investigation. For α-styryl triflate, the product study is complete and only kinetic work is now necessary.

In conclusion, we will obtain a broad picture of the vinyl cation mechanism via adjustments in the leaving group (Br-, -OTf, or the α-substituents, aryl, alkyl, alkyl rearranging systems).

Experimental

Characterization Techniques

All boiling points are uncorrected. (1)H NMR Spectra were recorded on a Varian FT 80-A Spectrometer. Chemical shifts are recorded in parts per million (ppm) from tetramethylsilane. Infrared spectra were obtained on a Perkin-Elmer Model 337 Spectrophotometer. Glc was performed on a Hewlett-Packard Model 5710A gas chromatograph with a Hewlett-Packard 3380S Peak Integrator equipped with flame ionization detector using a .125 in. x 10 ft. 15% THEED on 100/120 Chromosorb WAW column (column temperature 90°).

Materials

Trifluoromethanesulfonic acid was purchased from 3M Company as Fluorochemical Acid FC-24 and used without further purification. 3,3-Dimethyl-1-butyne was purchased from Aldrich Chemical Company. D_2O was purchased from Bio-Rad. Pentane, purchased from Fisher Scientific Company, was distilled over CaH_2.

Ethanol was obtained from U.S. Industrial Chemicals Company and used as purchased.

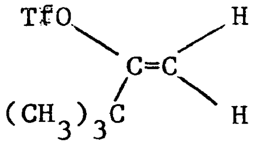
3,3-Dimethyl-1-buten-2-yl Triflate (1) [8]

3,3-Dimethyl-1-butyne (3.404 g, 0.040 moles) in 34 ml of dry pentane, (distilled over CaH_2) was stirred at -22°C as trifluoromethanesulfonic acid, (2 ml, 0.020 moles), in 34 ml of dry pentane was added over a period of three hours. The first drop of acid gave an intense red-orange color. After three hours of continuous stirring, the reaction was warmed to 0°C, carefully washed twice with 10 ml of saturated NaHCO solution, and dried over $MgSO_4$. The filtrate was concentrated by allowing a nitrogen gas stream to blow gently across the surface. The residue was immediately vacuum distilled to give 0.195 g (14.8%) of 3,3-dimethyl-1-buten-2-yl triflate (bp. 38-40°C; 9 mmHg) [9]. (1)H NMR ($CDCl_3$) 1.20 (s, 9H, t-Bu), 4.91 (d, J= 4.0 Hz., 1H, vinyl H trans to OTf), 5.03 (d, J= 4.0 Hz., 1H, vinyl H cis to OTf); IR (neat) 1655 (C=C), 1415, 1241, 1208, 1144, 1109, 1026, 941, 921, and 888 cm .

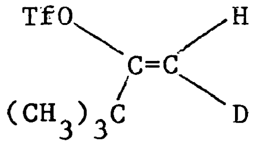
A very quick workup is necessary for this compound. The yield declines if not distilled in the same day.

(E)- and (Z)- 2-Deuterio-3,3-Dimethyl-1-buten-2-yl Triflate (2), (3)

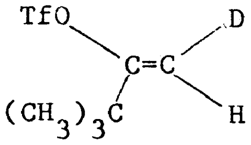
3,3-Dimethylbutyne-1-d [8] (3.403 g, 0.040 moles) and triflic acid (2 ml, 0.020 moles) gave an inseparable mixture of the (*E*)- (60.1%) and (*Z*)- (25.8%) d(1)-isomers. (1)H NMR ($CDCl_3$) 5.04 (d, 1H, J= 4.0 Hz., vinyl H cis to OTf), 4.94 (d, J= 4.0 Hz., 1H, vinyl H trans to OTf), 1.18 (s, 9H, t-Bu). Vinylic proton ratios of 9:1.88 indicating 85.9% d(1) products and 14.1% d(o) products.



(1)
14.1%



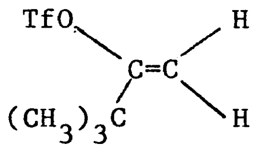
(2)
60.1%



(3)
25.8%

3,3-Dimethylbutyne (3.404 g, 0.04 moles) and triflic acid-d (3.0 g, 0.02 moles) gave inseparable mixture of the (*E*)-isomer (6%), (*Z*)-isomer (14%), and 3,3-dimethyl-1-buten-2-yl triflate (80%). (1)H NMR ($CDCl_3$) 1.18 (s, 9H, t-Bu), 5.04 (d, 1H, J= 4.0 Hz., vinyl H cis to OTf), 4.94 (d, J= 4.0 Hz., 1H vinyl H trans to OTf).

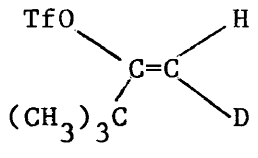
Vinylic proton area ratio 9:1.80 indicating 20% d(1) products and 80% d(o).



(1)

80%

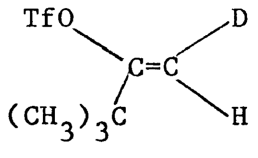
(E)



(2)

6%

(Z)

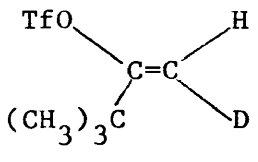


(3)

14%

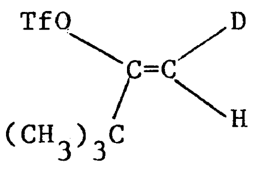
2,2-Dideuterio-3,3-Dimethyl-1-buten-2-yl Triflate (4)

3,3-dimethylbutyne-d (3.404 g, 0.04 moles) and triflic acid-d (3.0 g, 0.02 moles) gave an inseparable mixture of the d(2) product (57%), (E)- isomer (30.5%) and (Z)-isomer (12.4%) vinyl proton ratio 9:1.15 indicates 42.9% d(1) products [8]. No coupling of the vinylic protons was observed indicating no d(o) products.



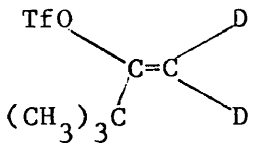
(E)

30.5%



(Z)

12.4%



(4)

57%

*Note

(E)- and (Z)-2-Deuterio-3,3-dimethyl-1-buten-2-yl triflate (2) and (3) were also allowed to react using the same procedure without solvent. Similar yields were observed.

3,3-Dimethylbutyne-1-d [55]

A mixture of (20 g, 0.25 moles) of 3,3-dimethylbutne, 50 ml of pyridine (dried over BaO, stored over CaH_2), 50 ml D_2O, and 0.33 g of sodium methoxide was shaken in a sealed "Pop" bottle for four days. The acetylene was isolated by simple distillation giving 15.7 g (78.5%). (1)H NMR ($CDCl_3$) 1.24 (s, 9H, t-Bu).

Trifluoromethanesulfonic Anhydride [56]

To a dry 100 ml round-bottom flask was added trifluoromethanesulfonic acid (36.3 g, 0.242 mole) and phosphorus pentoxide (27.3 g, 0.192 mole). The flask was stoppered and allowed to stand at room temperature for at least 3 hours. During this period, the reaction mixture changed from a slurry to a solid mass. The reaction mixture was then distilled at atmospheric pressure until no more crude triflic anhydride distilled, (b.p. 79-85 °C). The yield of the crude anhydride was 25.2 g (74%). The remaining acid was removed from the anhydride by the following procedure. A slurry of phosphorous pentoxide (2.6 g, 0.018 moles) in crude anhydride (25.2 g, 0.089 moles) is stirred at room temperature for 18 hours. The anhydride is distilled to give 22.6 g of triflic anhydride, (b.p. 81-84 °C). The above purification procedure is repeated to give 20.0 g of the pure triflic anhydride, (b.p. 81- 84 °C).

Trifluoromethanesulfonic Acid-d [56]

2.9 g (0.010 moles) portions of trifluoromethanesulfonic anhydride were sealed in ampules with 0.2 g D_2O. The ampoules were shaken daily until the mixture became homogenous (3-5 days) and were left out an additional week at room temperature before use.

Product Studies

In each experiment, *α*-t-butylvinyl triflate (23 mg., 0.1 mmole) in 5 ml of solvent buffered with 1,8-bis(dimethylamino)-naphthalene (21.4 mg, 0.1 mmole) was allowed to react at 64°C for at least four half-lives. 5 ul samples taken directly from the solvolysis mixture were analyzed by Glc. Elimination and substitution products showed to be stable under the solvolytic conditions as well as on the Glc column.

DISCUSSION

Trifluoromethanesulfonic Acid Addition to 3,3-Dimethyl-butyne

Electrophilic addition to alkynes can follow either an Ad(E)2 or Ad(E)3 mechanism. Under conditions of low reactivity [52] such as HCl or HOAc, one typically observes alkynes having exclusive alkyl substitution react via Ad(E)3 with predominant anti addition.

Trifluoromethanesulfonic acid (triflic acid) is a strong acid. The triflate anion is a weak nucleophile. Hence, preferential formation of ionic intermediates is more likely to occur in the addition of triflic acid as compared to an addition by a weaker acid. Thus, an Ad(E)2 mechanism is postulated and has been verified by similar aryl substituted alkynes such as phenylacetylene [49].

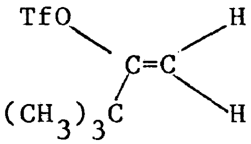
The product ratios should be easily predicted for a linear vinyl cation intermediate (syn/anti; 50:50). Previous work by Sivavec [57] with addition of TfOH to phenylacetylene resulted in preferential anti addition (56% with TfOH and 60% with TfOD). A hydrogen bridged intermediate was proposed [49] to account for 20% of the anti product since syn addition was also observed, the remaining 80% of the "bridged" vinyl cation intermediate collapsed to the free vinyl cation providing a syn to anti ratio of 50:50. The anti to syn ratio is reduced compared to the values reported by Olah and Spear [49] (anti/syn; 6.75:1.0) in fluorosulfonic acid addition to 2-butyne. Such discrepancy may be accounted by the fact that phenyl substituted alkynes with CF SOH possess enhanced stability compared with the hydrogen-bridged alkyl substituted alkyne due to charge delocalization. Therefore, escape to the completely dissociated free ion pair should occur more readily and the cation should then react as a free linear vinyl cation.

Consider the results obtained from the addition of triflic acid to 3,3-dimethylbutyne-d and triflic acid-d to 3,3-dimethylbutyne Table(XI).

Table(XI)

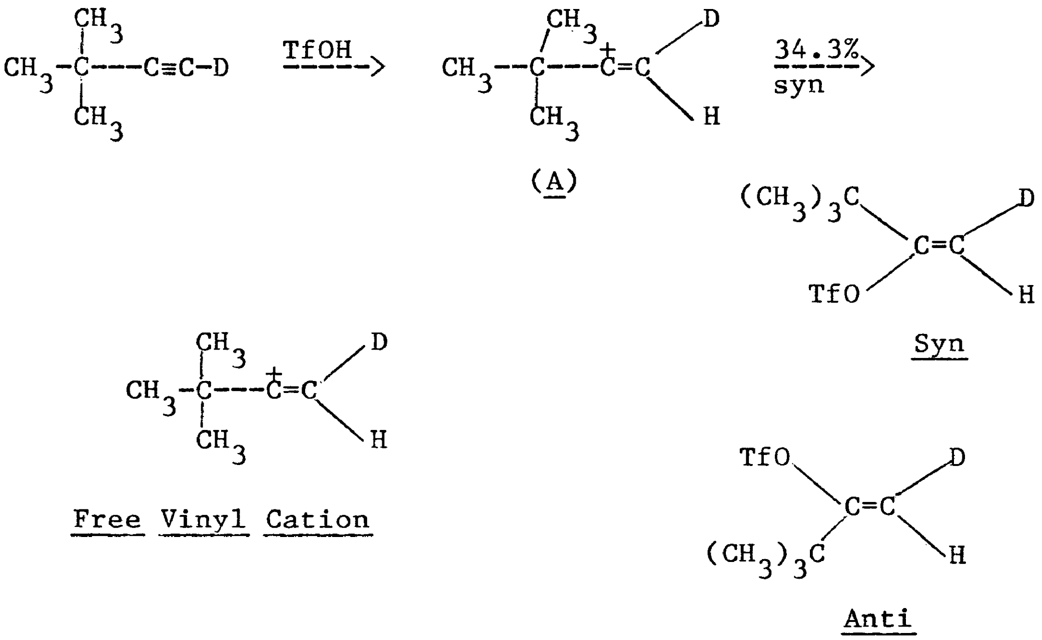
3,3-Dimethylbutyne	Triflic Acid	% Syn Addition	% Anti Addition	%d(o)
$(CH_3)_3CC{\equiv}CH$	TfOD	14.0	6.0	80.0
$(CH_3)_3CC{\equiv}CD$	TfOH	60.1	25.8	14.1

(d(o))



This is a completely different picture from the phenylacetylene for syn predominates. Preferential syn additions have been observed in the additions of acid halides like HBr to α-anisyl-β-deuteroacetylene [48] and HCl to phenylacetylene [58]. Such syn predominance has also been observed in solvents of low dielectric constants (dichloromethane, acetic acid) [48]. Syn addition has also been observe in the addition of triflic acid to 1-hexyne, propyne, and 1-butyne (syn/anti; 4:1) [49]. One can rule out the possibility of acid catalyzed isomerization between the cis and trans adducts, and the deuteration experiments demonstrated the irreversibility of the reactions.

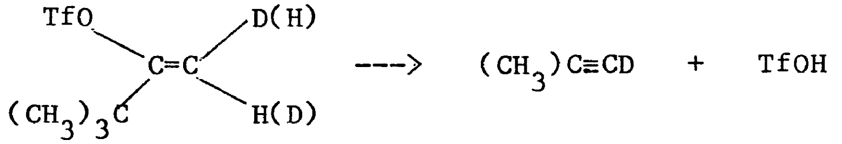
One can interpret the results in the following way Figure(40). Consider the addition of TfOH to 3,3-dimethylbutyne-d. Two intermediates must be in competition. For intermediate (A), a methyl bridge formed during the tight ion pair hinders the (TfO-) anion from an anti attack. Hence, preferential syn addition takes place. This is not unreasonable since the α-t-butylvinyl cation is noted for rearrangements of its methyl group [7].



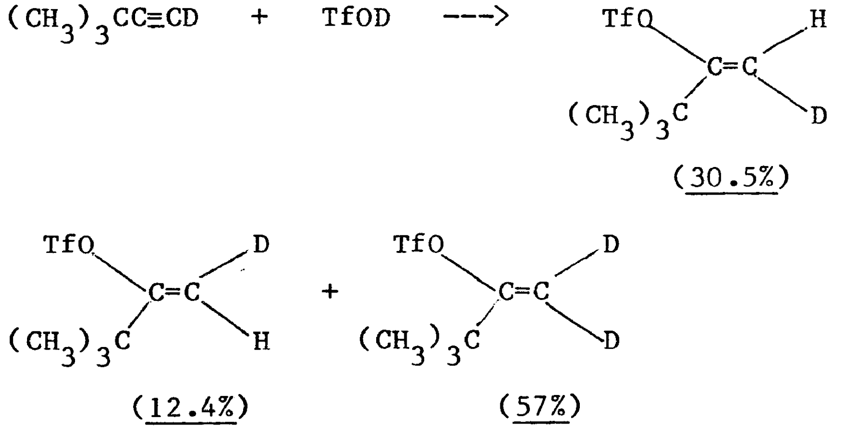
The remaining 51.6% of intermediate (A) dissociates to a linear free vinyl cation (B) where symmetric additon takes place. This accounts for the anti addition product and an increase in the syn adduct.

The loss of deuteration, i.e., the formation of the d(o) compound, is now under current investigation. The predominance of d(o) in the addition of TfOD to 3,3-dimethylbutyne cannot be explained in the following ways. The possibility of solvent contamination was ruled out by running the reaction "neat". Similar ratios of deuterium incorporation were obtained. A contamination in the TfOD was dismissed, for the same starting acid procured 100% substituted d(1) adducts upon the addition of

2-butyne. Furthermore, a competing elimination reaction by the d(1) adducts Figure(41) was ruled out by the presence of 42.9% d(1) compounds from the reaction presented in Figure(42).



(41)



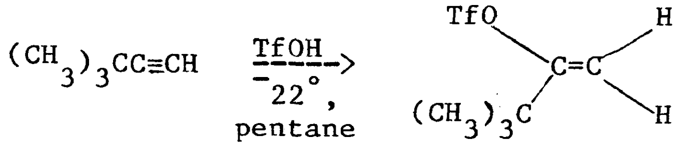
(42)

Although further verification is needed, it appears as if the "mysterious" source of protons may be from (H+) elimination subsequent to rearrangements within the vinyl cation intermediate.

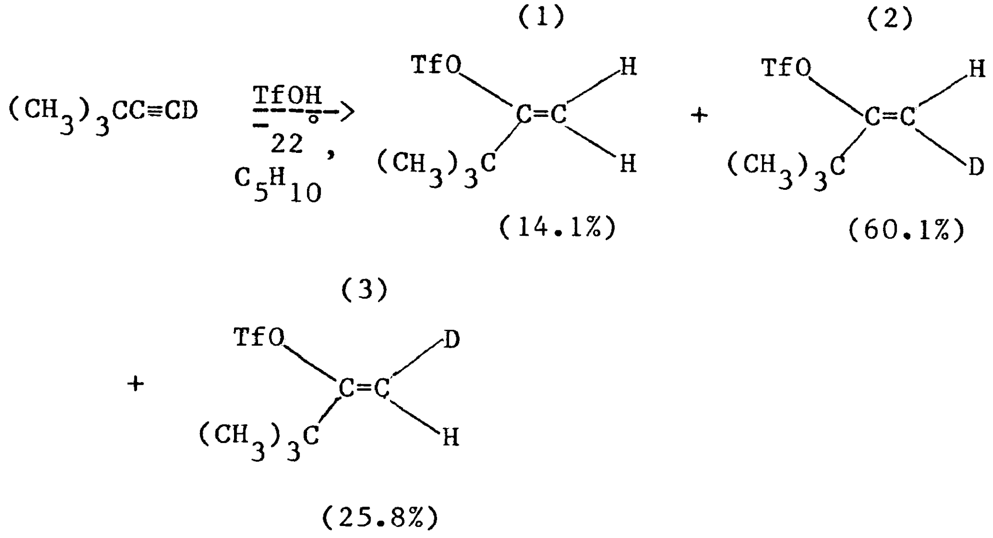
Solvolytic Product Studies of a-t-Butylvinyl Triflate

The solvolysis studies of _-*t*-butylvinyl triflate in coordination with future kinetic studies will contribute to the "pyramid of knowledge" in unraveling the mechanistic mystique of alkyl substituted vinyl triflates. Previous product studies have been limited and rate analyses are virtually nonexistent. Synthesis of α-*t*-butylvinyl triflate (1) and its deuterio (2), (3), and dideuterio (4) analogues by the addition to *t*-butylacetylene and *t*-butylacetylene-d to triflic acid and triflic acid-d, *cis* and *trans*, deuterium isotope effects in product studies and from future kinetic studies may be calculated (Equations 1-4) (see Appendix I).

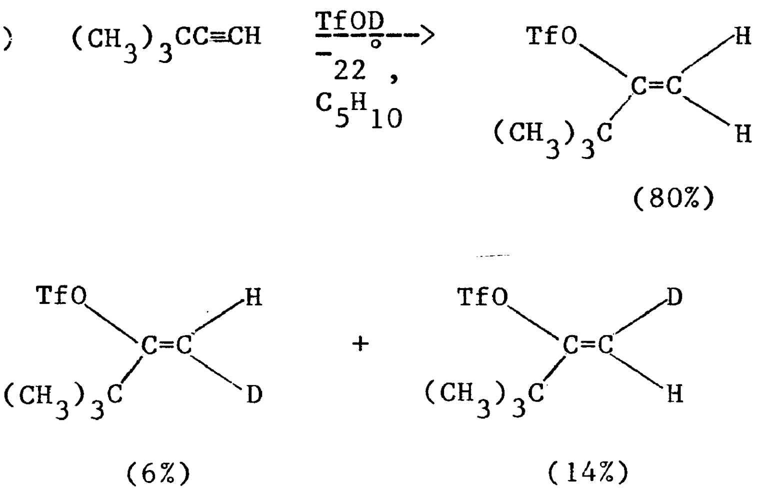
(1)



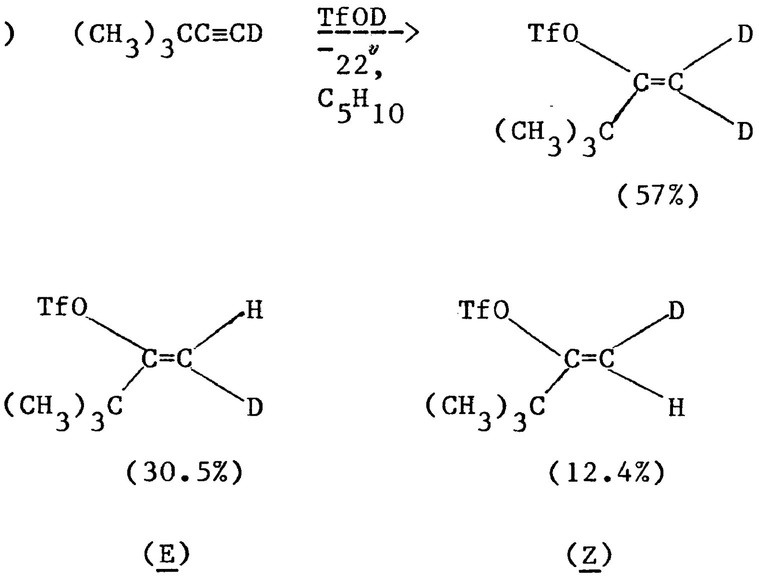
(2)



(3)


(CH3)3CC≡CH
TfOD
-22°,
C5H10
TfO
C=C
H
H
(CH3)3C
(80%)
TfO
H
D
(6%)
+
D
H
(14%)

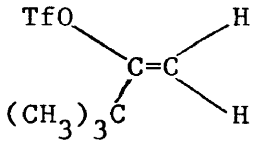
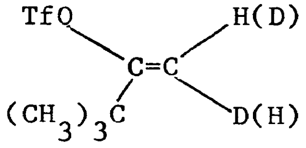
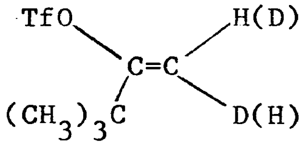
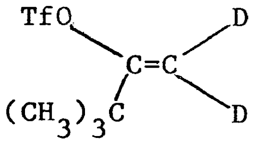
(4)


(CH3)3CC≡CD
TfOD
-22°,
C5H10
TfO
C=C
D
D
(CH3)3C
(57%)
H
D
(30.5%)
(E)
D
H
(12.4%)
(Z)

The parent compound d(o), the (E) and (Z) deuterio-d(1) and dideuterio-d(2) analogues cannot be separated by preparative gas chromatography, yet a product analysis can be obtained by from the (1)H NMR determined composition of the inseparable mixture. Glc-Mass spectral analysis was not possible owing to the high thermal instability of the α-t-butylvinyl triflate.

The product composition of 3,3-dimethylbutyne in solvolysis of the α-t-butylvinyl triflates in ethanol-water and in trifluoroethanol-water solvents at 64 °C was determined by Glc using a 0.125 in. x 10 ft. THEED on 100/120 Chromosorb WAW column and flame ionization detector Table(XII).

Product Studies;
Composition of Alkyne(%)
Table(XII)

Compound	Solvent	Temp °C	Hours of Reacting Time	%Alkyne
	60/40 E/W	64.2	5.16	74.4
	70/30	64.2	9.46	75.2
	80/20	64.2	24	74.0,70.0
	97 TFE	64.2	9.46	8.6,29.0,19.6
	60/40 E/W	64.2	5.16	56.1,66.6
	70/30	64.2	9.46	53.9,57.3
	80/20	64.2	24	46.7,59.5
	97 TFE	64.2	9.46	9.6
from TfOH				
	60/40 E/W	64.2	5.16	60.6,74.2
	70/30	64.2	9.46	77.6,80.8,77.3
	80/20	64.2	24	71.3,82.0
	97 TFE	64.2	9.46	22.7,21.1
from TfOD				
	60/40 E/W	64.2	5.16	63.0,50.0
	70/30	64.2	9.46	62.0,61.4,40.4
	80/20	64.2	24	60.8,49.3
	97 TFE	64.2	9.46	8.7,13.5

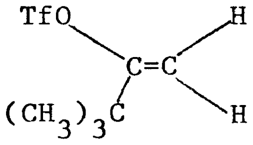
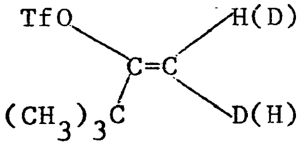
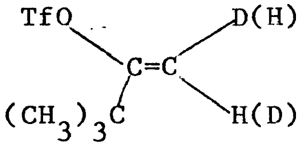
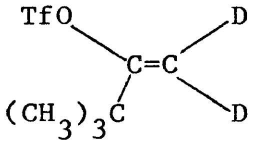
* All runs; percent taken out of all substitution and rearranged products in different solvents.

Since the results in the various Ethanol/W and TFE/W solvents are virtually the same, within their respected media, and within experimental error, one may compile the various concentrations into one general table of averaged values obtained in EtOH/W and

TFE/W solvents Table(XIII).

Table(XIII)

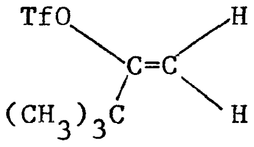
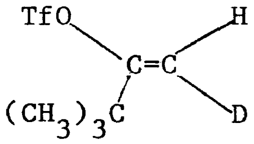
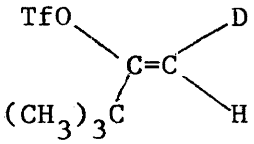
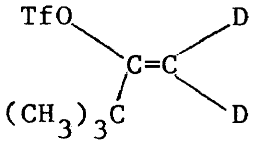
Total Average Percent Alkyne (3,3-Dimethylbutyne-(d))

	EtOH-W	97 TFE-W
	73.5	22.0
 from TfOH	56.7	9.6
 from TfOD	74.2	21.0
	55.4	11.1

Consider the results of Table(XIII). The data provide information that is not unexpected. Compound (1) and (3) are similar in the amount of elimination. This is expected since (3) is 80% of the d(o) adduct Table(XIV).

Table(XIV)

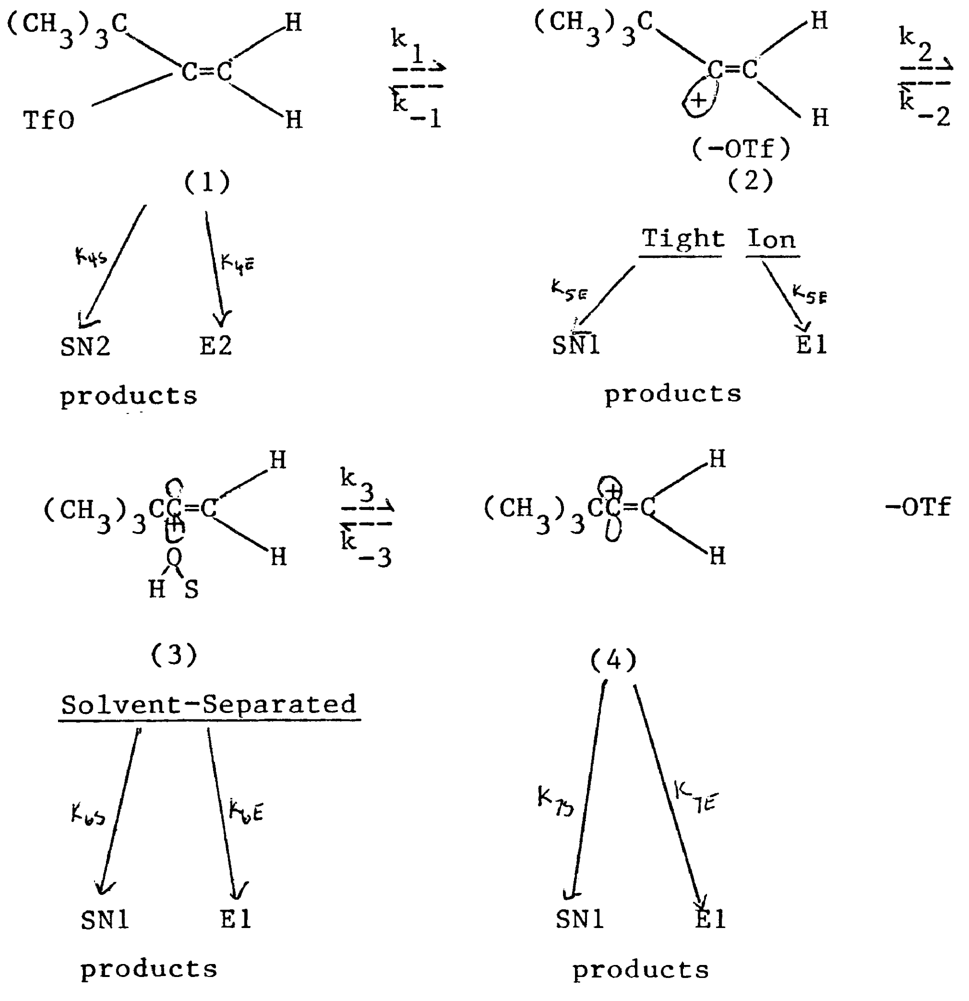
Purity of the Starting Triflates

	Compound			
	(1)	(2)	(3)	(4)
	100	14.1	80.0	---
 (E)	---	60.1	6.0	30.5
 (Z)	---	25.8	14.0	12.4
	---	---	---	57.0

One can further see evidence for deuterium isotope effects as exhibited by the reduction of elimination in going from d(o) to d(1) compound (2) to d(2) adducts. It is relatively easier to eliminate a (H) rather than a deuterium. Furthermore, there is more elimination in the Ethanol-W solvent as compared to the 97

TFE-W mixture.

The point of interest, is comparing the large percent elimination values in the EtOH-W solvent to the depressed values in the TFE-W media. Recalling Winstein's ion pair scheme, one may explain the data in the following way Figure(43).



Both concerted elimination (E2) and direct displacement (SN2), may be dismissed. The concentration of buffer does not affect the percent elimination. A "super" leaving group, such as the triflate anion, promotes an intermediate type that is more dissociated than (1). If the amount of elimination in the nucleophilic EtOH/W solvent was less than the weakly nucleophilic TFE/W solvent within experimental error, then the proposal of a tight ion pair intermediate would be a reasonable assumption. The vinyl cation intermediate would be independent of solvent ionizing power. However, the results from Table(XIII) prompt a different picture, a solvent-separated intermediate.

In the relatively nucleophilic EtOH-W solvent, the rate determining step may be assumed to be the solvent-separated ion pair. This is reasonable since the leaving group (TfO-) readily eliminates allowing the cation to be solvated. From Figure(43), one observes that such a rate determining intermediate may exploit the competition between elimination or substitution products. For EtOH-W solvent, percent elimination far surpasses percent substitution.

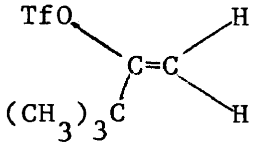
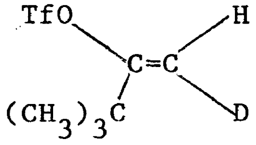
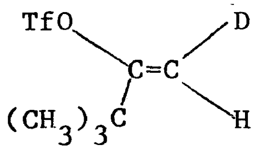
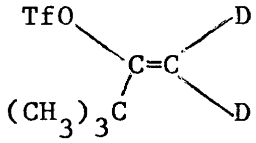
In 97 TFE-W solvent a less polar solvent than EtOH-W but of approximately the same ionizing power as 60/40 EtOH-W, one observes a decrease in the percent elimination relative to substitution and rearranged products. Such is consistent with competition between substitution and elimination mechanism from the solvent-separated ion pair. Upon further decrease in polarity and an increase in basicity, as in HFIP (hexafluoroisopropyl alcohol) solvent, one might predict an ever smaller percent elimination and more substituted and rearranged products.

One interpretation of the difference between percent substitution versus elimination in 97 TFE-W and EtOH-W solvents may be explained by comparing the relative basicities of the solvents in the solvent-separated ion pair. The more basic EtOH-W induces more elimination from the solvent-separated intermediate. The less basic 97 TFE-W solvent encourages more substitution and rearranged products than elimination. These results are not unusual in that similar findings have been observed in α-styryl triflate product studies [56].

Further evidence for a solvent-separated vinyl cation intermediate stems from product isotope effect calculations. Consider Table(XV), where percent elimination has been presented for each compound.

Table(XV)

% Elimination for each Respective Compound

	73.5	22.0
 (E)	36.6	0.47
 (Z)	94.3	24.1
	57.1	13.9

* Sample calculation performed in Appendix I

The ratio K(H)/K(D) was computed from the percent (H) and percent (D) elimination for both anti and syn elimination Table(XVI).

Table(XVI)

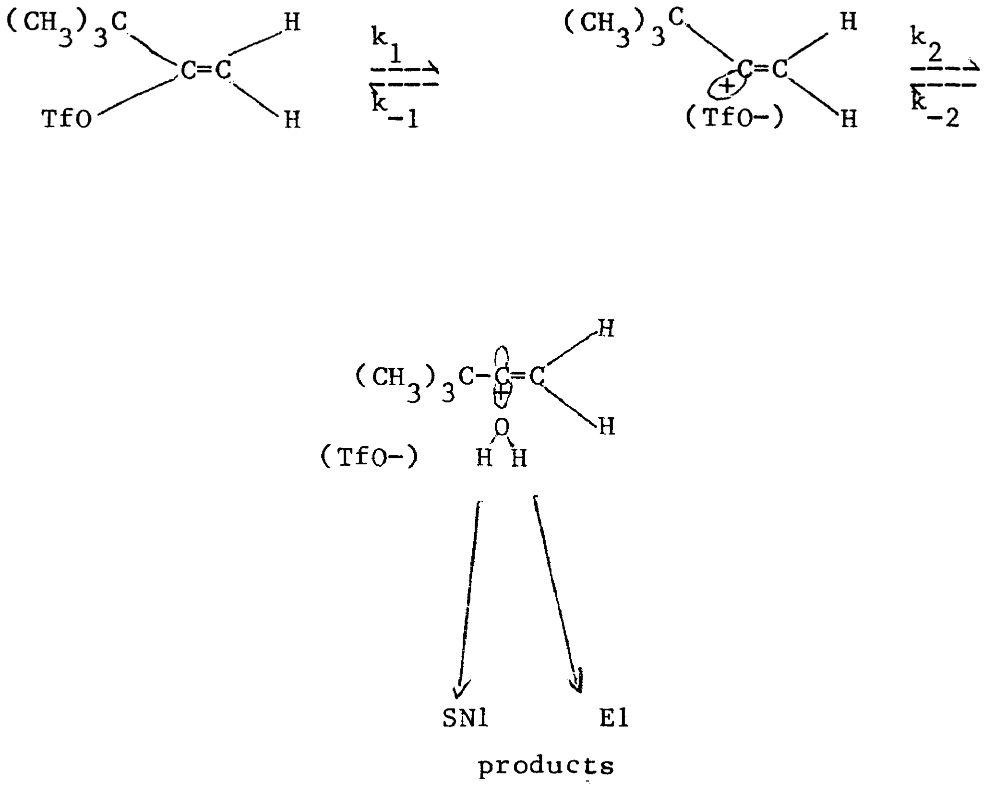
k_H/k_D	EtOH-W	TFE-W
Anti	1.29	1.60
Syn	1.29	1.61

Interestingly, the results all show 2° isotope effects with a small amount of 1° isotope effect involved. Such results also may help dispel any thought of elimination from the starting vinyl triflate if a 1° isotope effect had been observed, then the starting material would have been the source of elimination. Furthermore, the ratios of anti to syn in both solvents is nearly one, providing evidence for a symmetrical intermediate. The intermediate comes from a linear solvent-separated ion pair rather than a bent tight ion pair that would result in preferential elimination.

Finally, a qualitative picture of the transition state can be proposed. From the evidence thus far, a high energy transition state with little stretching of the C-H(D) bond is most probable.

The elimination product is formed by a trans H(D) or a cis H(D) elimination from the vinyl cation. Further study is needed using mass spectral analysis of the t-butylacetylene isolated after the solvolysis in several solvents to determine the ratio of anti to syn elimination and characterization of the relative amounts of t-butylacetylene and t-butylacetylene-d.

In summary, the abbreviated reaction Figure(44), should apply for EtOH-W and TFE-W solvolysis of α-t-butylvinyl triflate.


(CH3)3C
TfO
H
H
k1
k-1
(CH3)3C
(TfO-)
H
H
k2
k-2
(CH3)3C
(TfO-)
H
H
O
H H
SN1
E1
products

Summary

Much work is still necessary for a thorough understanding of *α*-*t*-butylvinyl triflate. Qualitative statements must be coupled with quantitative work. More specifically, consider future work for a conclusive product study.

In our solvolysis studies, with the aid of gas chromatography, we were able to identify the *t*-butylacetylene and 3,3-dimethyl-2-butanone compounds via spiking the solvolysis mixture with samples of ketone and alkyne. Yet, there are three to four peaks that have not been positively identified. Two of the peaks are probably 2,3-dimethyl-1,3-butadiene (1) and the ethanol substituted ether product (2). Conceivably, the ethanol could substitute after the 1,2 methyl shift giving a second structural ether (3) [7].

Mass spectral analysis or spiking the solvolysis mixture with known samples of the three compounds, identifiable by G.C.analysis, will sort out labeling difficulties from solvolysis products.

Mass spectral analysis is also necessary to determine whether or not deuterium is in the elimination product from the solvolysis of the *E* and *Z* isomers of *α-t*-butylvinyl triflate. This result would tell us whether we are getting preferential *syn* or *anti* elimination, without solving simultaneous equations.

In the making of the starting triflate compounds, a new mode of reaction conditions should be explored. The best yield (%) was never more than 15%. This low yield may come from vacuum distilling at a rapid rate with too high a "pot" temperature (above 60'C). The problem may also lie not in the workup but in the synthesis step. It is my belief that the workup has only a minor contribution to a poor yield. The reaction pot is forming a vinyl cation that will hopefully react with the triflate anion. In the addition of *t*- butylacetylene and TfOD we get a large percentage (80%) of the d(o) adduct. This information coupled with low yields and possible acid catalysis leads one to perceive a reaction pot full of rearranging cations, methyl shifts and possible proton eliminations and reattacking at different points on the molecule. All is speculation, but perhaps the addition of TfOD to $(CD)_3C-C=C-H$ will tell us whether the d(o) adduct is being formed from a hydrogen in one of the methyl groups of the *t*-butyl portion of the acetylene molecule.

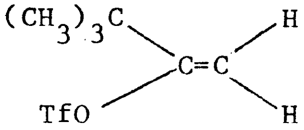
In obtaining accurate results from G.C.analysis of the solvolysis studies, it is necessary to cool the ampoule after it has been removed from the hot oil bath (62'C) so that upon opening, the volatile material will not escape The method of allowing it to cool, event to -10'C, is not satisfactory. An ampoule that had a "septum" like top would prevent any escape of volatile product and thus a more accurate result.

Rate studies are also necessary to verify the product isotope effects observed in present experiments. Such information would defend a solvent-separated ion pair intermediate.

Appendix I

Sample calculation of Fraction Elimination in 3,3-dimethyl-1-buten-2-yl triflate, (E)- and (Z)-2-deuterio-3,3-dimethyl-1-buten-2-yl triflate, and 2,2-dideuterio-3,3-dimethyl-1-buten-2-yl triflate from Total Average Percent Alkyne (60%, 70%, 80%, (vol.) E-W).

$(CH_3)_3CC{\equiv}CH$ + TfOH --->



(d_o)

$$F_{\text{elim obsd}} = .735$$

(A) $(CH_3)_3CC{\equiv}CD$ + TfOH ---> (Z)-isomer + (E)-isomer

25.8% 60.1%

+ d_o

14.1%

$$F_{\text{elim obsd}} = (\text{Fraction H,H})F_{\text{H elim}} \quad F_{\text{Z elim}}(\text{Fraction Z})$$

$$+ \quad F_{\text{E elim}}(\text{Fraction E})$$

$$(1) \quad .567 = (.141)(.735) + F_z(.258) + F_E(.601)$$

(B) $(CH_3)_3CC{\equiv}CH$ + TfOD ---> (Z)-isomer 14% + (E)-isomer 6%

+ d_o 80%

(2) .742 = .80(.735) + F_E(.o6) + F_Z(.14)

(C) $(CH_3)_3CC{\equiv}CD$ + TfOD ---> d_2 57% + (Z)-isomer 12.4%

+ (E)-isomer 30.5%

(3) .554 = .305F_E + .124F_z + .57$F_{D,D}$

Solving equations (1) and (2) simultaneously:

$$F_Z = .943$$

$$F_E = .366$$

Using (3), substitute for $F_{Z\ elim}$ and $F_{E\ elim}$. Solve for $F_{D,D}$

$$.544 = (.305)(.366) + .124(.943) + (.57)F_{D,D}$$

$$F_{D,D} = .571$$

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