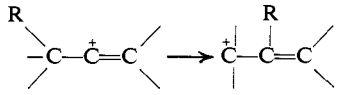
Communications to the Editor

Mechanism of Rearrangement across the Double Bond in Vinyl Cations Generated by Solvolysis. Evidence for a Vinylidene Phenonium Ion[1]

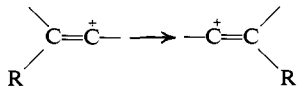
Sir:

One of the most characteristic properties of carbonium ions is their disposition and facility to undergo rearrangements such as hydride shifts, 1,2-alkyl migrations, Wagner–Meerwein and cyclopropylcarbinyl rearrangements, and others. Analogous vinyl cation[2] rearrangements may be classified into two broad categories: (1) migration to the double bond (**1a** → **1b**)



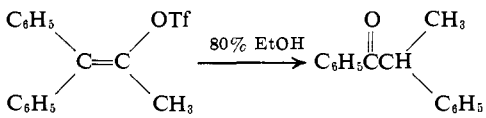
1a **1b**

and (2) rearrangement across the double bond (**2a** → **2b**). Examples of both types have been reported.[3]



2a **2b**

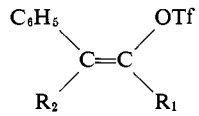
In particular, solvolysis of **3a** in 80% aqueous ethanol gave, besides a small amount of allene, exclusively the rearranged ketone **3b** as product.[3b] Two questions



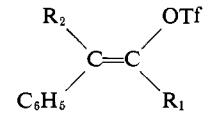
3a **3b**

can be asked regarding such a migration across the double bond. Is the rearrangement concerted, *i.e.*, synchronous ionization–migration, or nonconcerted, *i.e.*, ionization to a free vinyl cation first, then rearrangement? What is the stereochemistry of the rearrangement; is the substituent that is trans or the one that is cis to the leaving group the one that migrates? In order to answer these questions we prepared and investigated the solvolytic behavior of *cis*- and *trans*-3-phenyl-2-buten-2-yl triflates (**4** and **5**, respectively).

The parent triflates **4a** and **5a** were prepared from 3-phenyl-2-butanone according to the procedure of Dueber, *et al.*,[4] and were readily separated by prepara-



4a, $R_1 = R_2 = CH_3$
b, $R_1 = CD_3$; $R_2 = CH_3$
c, $R_1 = CH_3$; $R_2 = CD_3$



5a, $R_1 = R_2 = CH_3$
b, $R_1 = CD_3$; $R_2 = CH_3$
c, $R_1 = CH_3$; $R_2 = CD_3$

tive gas chromatography (15 ft × $^3/_8$ in., 15% SF-96, 160°) into the cis (**4a**) and trans (**5a**) isomers, respectively.[5] The α-CD_3 isomers[6] **4b** and **5b**[7] were similarly prepared and isolated from $(C_6H_5)CH_3CDC(=O)CD_3$, obtained by repeated exchange of 3-phenyl-2-butanone with D_2O catalyzed by small amounts of NaOD. The β-CD_3 isomers[6] **4c** and **5c**[7] were prepared from (C_6H_5)-$CD_3CHC(=O)CH_3$, obtained from alkylation of phenylacetone with CD_3I.

The rates and products of solvolyses of vinyl triflates **4a** and **5a** are summarized in Tables I and II, respectively. Products were identified by comparison of retention times with authentic samples as well as spectroscopically. Control experiments in 60% ethanol demonstrated that both products are stable to the reaction conditions. Similarly the products were found to be stable in TFE under the reaction conditions employed for the faster reacting trans isomer, but some rearrangement of the vinyl ether to allene and allene to dimer occurred for the much slower reacting cis isomer.

Since the parent system **4a** and **5a** is degenerate to rearrangement, deuterium labeling was employed to measure the extent of phenyl migration. Migration of a phenyl group across the double bond has the net effect of interchanging the α-CD_3 group with the β-CH_3 group in the product ketone and allene in aqueous ethanol in the **b** series and *vice versa* in the **c** series. The extent of rearrangement was determined by the nmr[8] as well as the mass spectra[9] of each of the products resulting from solvolysis for about 3 half-lives. Control experiments demonstrated that the β deuteriums of the product ketone exchanged less than 1–2% with solvent for the faster reacting trans isomers and less than 8–10% for the slower reacting cis isomers and the

(1) Paper VII in a series on the preparation and solvolysis of vinyl triflates. Paper VI: W. D. Pfeifer, C. A. Bahn, P. v. R. Schleyer, S. Bocher, C. E. Harding, K. Hummel, M. Hanack, and P. J. Stang, *J. Amer. Chem. Soc.*, 93, 1513 (1971). Presented at the 164th National Meeting of the American Chemical Society, New York, N. Y., Sept 1972.

(2) For reviews on vinyl cations see: (a) P. J. Stang, *Progr. Phys. Org. Chem.*, **10**, 276 (1973); (b) G. Modena and U. Tonellato, *Advan. Phys. Org. Chem.*, 9, 185 (1971); (c) M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1970); (d) H. G. Richey, Jr., and J. M. Richey, "Carbonium Ions," Vol. I, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1970.

(3) (a) A. G. Martinez, M. Hanack, R. H. Summerville, P. v. R. Schleyer, and P. J. Stang, *Angew. Chem., Int. Ed. Engl.*, 9, 302 (1970); (b) M. A. Imhoff, R. H. Summerville, P. v. R. Schleyer, A. G. Martinez, M. Hanack, T. E. Dueber, and P. J. Stang, *J. Amer. Chem. Soc.*, 92, 3802 (1970).

(4) T. E. Dueber, P. J. Stang, W. D. Pfeifer, R. H. Summerville, M. A. Imhoff, P. v. R. Schleyer, K. Hummel, S. Bocher, C. E. Harding, and M. Hanack, *Angew. Chem., Int. Ed. Engl.*, 9, 521 (1970); P. J. Stang and T. E. Dueber, *Org. Syn.*, submitted for publication.

(5) Stereochemistry was assigned on the basis of chemical shifts and coupling constants. For **4a** nmr (CCl_4) δ 2.02 (m, 3, β-CH_3), 2.17 (m, 3, α-CH_3), 7.13 (br s, 5, C_6H_5); **5a** (CCl_4) δ 1.97 (m, 3, α-CH_3), 2.09 (m, 3, β-CH_3), 7.24 (m, 5, C_6H_5). For the cis isomer **4a** the long-range coupling between the methyls is much less pronounced and resolved ($^5J \simeq$ 0.9 Hz) than for the trans isomer **5a** ($^5J \simeq$ 1.3 Hz). See P. Laszlo and P. J. Stang, "Organic Spectroscopy: Principles and Applications," Harper and Row, New York, N. Y., 1971, and references therein.

(6) For **4b** nmr (CCl_4) δ 1.98 (s, 3, CH_3), 7.06 (br s, 5, C_6H_5); **4c** (CCl_4) δ 2.10 (s, 3, CH_3), 7.10 (br s, 5, C_6H_5); **5b** (CCl_4) δ 2.09 (s, 3, CH_3), 7.16 (m, 5, C_6H_5); **5c** (CCl_4) δ 1.96 (s, 3, CH_3), 7.16 (m, 5, C_6H_5).

(7) In the preparation of the trans deuterio isomers **5b** and **5c** from the respective ketones some (15–25%) deuterium scrambling (*i.e.*, formation of some **5c** along with **5b** and *vice versa*) occurred. No such rearrangement was observed in the preparation of the cis isomers **4b** and **4c**. This scrambling during the preparation of only the trans isomers is itself indicative of phenyl participation.

(8) Nmr $(C_6H_5)CH_3CHC(=O)CH_3$ (CCl_4) δ 1.26 (d, β-CH_3), 1.90 (s, α-CH_3).

(9) The base peak for $(C_6H_5)C(CH_3)HC(=O)CH_3$ is at m/e 105 corresponding to the methyl tropylium ion. Phenyl migration in the ketone could therefore be readily and accurately determined by the 108/105 ratio unaffected by any exchange with solvent in the β position. The mass spectral and nmr analyses were, within experimental error, identical. The migration in the allene product was similarly determined from the M − 15 and M − 18 ratios.

Table I. Rates of Reaction of Vinyl Triflates **4a** and **5a**

Compd	Solvent	Temp, °C	k, sec^{-1} [a]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
4a	60% EtOH	25.0[b]	3.71×10^{-9}	29.3	1.3
		74.96	$(5.22 \pm 0.23) \times 10^{-6}$		
		99.81	$(9.30 \pm 0.24) \times 10^{-5}$		
	97% TFE[c]	25.0[b]	1.12×10^{-8}	24.2	−13.6
		85.02	$(1.29 \pm 0.03) \times 10^{-5}$		
		99.97	$(4.86 \pm 0.22) \times 10^{-5}$		
		120.0	$(2.87 \pm 0.07) \times 10^{-4}$		
5a	60% EtOH	25.0[b]	1.12×10^{-7}	27.6	2.2
		74.96	$(1.04 \pm 0.01) \times 10^{-4}$		
		99.86	$(1.58 \pm 0.01) \times 10^{-3}$		
	97% TFE[c]	25.0[b]	1.07×10^{-6}	22.7	−9.6
		74.96	$(3.04 \pm 0.02) \times 10^{-4}$		
		90.52	$(1.27 \pm 0.02) \times 10^{-3}$		
		99.88	$(2.90 \pm 0.09) \times 10^{-3}$		

[a] Rates were measured conductometrically (0.6 μl/10 ml) buffered with pyridine and are averages of three–five determinations. In all cases, excellent first-order rates were observed for more than 94% reaction. [b] Extrapolated from higher temperatures. [c] 97.09 wt % trifluoroethanol–water.

Table II. Products of Reaction of Vinyl Triflates **4a** and **5a**

Compd	Reactn Condn [a]	$C_6H_5C(CH_3)H$—C(=O)CH_3, %	$C_6H_5C(CH_3)$=C=CH_2, %	$C_6H_5C(CH_3)$=CCH_3-(OCH_2CF_3), %
4a	60% EtOH, 75°	33.5	66.5	
	Abs TFE, 85° [b]	Trace	23.3	76.7[c]
5a	60% EtOH, 75°	82.0	18.0	
	Abs TFE, 85°		6.7	93.3

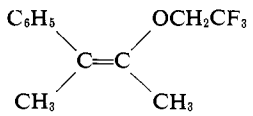
[a] Buffered with 1.1 equiv of pyridine. [b] Trace amounts, <1% of an unidentified product was also observed. [c] At ~25% reaction.

Table III. Rearrangement and Stereochemistry of the Products in the Reaction of Vinyl Triflates **4** and **5**

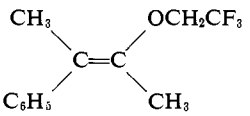
Compd	Reactn Condn[a]	D_3C(O)$C_6H_5CHCCH_3$, %	H_3C(O)$C_6H_5CHCCD_3$, %	H_3C-C_6H_5C=C=CD_2, %	D_3C-C_6H_5C=C=CH_2, %	**6a**	**6b**
4b	60% EtOH, 75°	34.5 ± 0.4	65.4 ± 0.4	72.7 ± 0.6	27.3 ± 0.6		
4c	60% EtOH, 75°	65.5 ± 0.4	34.5 ± 0.4	*b*	*b*		
4a	Abs TFE, 85°					3.6 ± 0.2	96.4
5a	Abs TFE, 85°					0.55 ± 0.05[c]	99.5
5b	60% EtOH, 75°	47.6 ± 0.3	52.3 ± 0.3	*b*	*b*		
5c	60% EtOH, 75°	51.5 ± 0.7	48.6 ± 0.7	41.1 ± 0.7	58.9 ± 0.7		

[a] Buffered with pyridine. [b] Not determined. [c] Average of two determinations at each of 10, 25, and 99% reaction. Analyzed on a 20 ft × 1/8 in. 5% SF-96 column at 95° with a flame ionization detector gc. *Extreme* care must be taken not to overload the column or some (1–5%) rearrangement of the trans to cis vinyl ether may occur.

γ deuteriums of course did not exchange at all. The results are shown in Table III. Another approach to the question of participation involves examination of the product stereochemistry in nonaqueous solvent. Therefore, the stereospecificity of solvolysis of **4a** and **5a** was determined in absolute trifluoroethanol (TFE) by a careful examination of the amounts of cis (**6a**) and trans (**6b**) vinyl ethers formed from each of the stereo-



6a



6b

isomeric vinyl triflates.[10] These results are also shown in Table III.

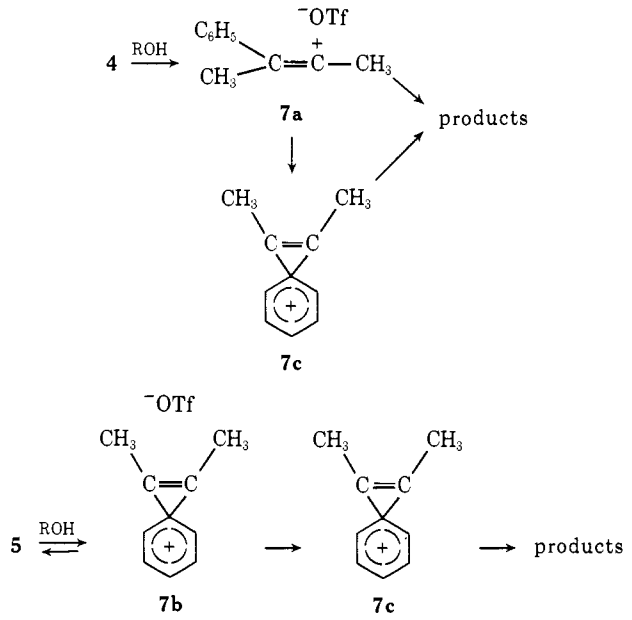
(10) Stereochemistry was assigned on the basis of chemical shifts and coupling constants. For **6a** nmr (CCl_4) δ 1.90 (s, 6, 2-CH_3), 3.50 (q, 2, CH_2, J_{HF} = 8.3 Hz), 7.02 (m, 5, C_6H_5); (C_6H_6) δ 1.65 (q, 3, CH_3, ^5J = 0.9 ± 0.1 Hz), 1.71 (q, 3, CH_3, ^5J = 0.9 ± 0.1 Hz), 3.38 (q, 2, CH_2, J_{HF} = 8.3 Hz); **6b** nmr (CCl_4) δ 1.77 (q, 3, CH_3, ^5J = 1.3 ± 0.1 Hz), 1.98 (q, 3, CH_3, ^5J = 1.3 ± 0.1 Hz), 3.95 (q, 2, CH_2, J_{HF} = 8.5 Hz), 7.02 (m, 5, C_6H_5).

It is evident from the data presented that there are significant differences in the solvolytic behavior of *cis*-(**4**) and *trans*-3-phenyl-2-buten-2-yl triflates (**5**). In the trans isomer **5** the major product of reaction in aqueous solvent is the ketone and in absolute TFE the vinyl ether, whereas significant amounts of allene are formed in both solvents from the cis isomer **4**. The rate of the trans isomer **5** is 20-fold and 62-fold that of the cis isomer **4** in aqueous ethanol at 75° and 97% trifluoroethanol at 85°, respectively,[11] suggesting that the former, which is in a geometrically

(11) It is unlikely that this trans:cis rate ratio can be ascribed solely to ground-state energy differences of the starting isomeric triflates. Although so far we have been unable to find experimental conditions for direct equilibration of the isomeric vinyl triflates without decomposition, several indirect pieces of evidence, such as the ratio of formation of triflates from ketone (~75:25 trans:cis, presumably under thermodynamic conditions) and the partial equilibration of the corresponding vinyl acetates, indicate that the equilibrium is not far from 50:50 and may in fact, at least in polar solvents, be in favor of the trans isomer. It is even more difficult to ascertain differences, if any, due to transition-state effects such as the hindrance to leaving group departure by an adjacent cis phenyl rather than a methyl group. However, it is unlikely that such transition state effects alone could account for the rather large rate ratios observed.

favorable conformation (trans coplanar) for participation, reacts by such a pathway. This hypothesis is consistent with and strongly supported by the stereochemical data in Table III. Rearrangement is clearly indicated by the deuterium labeling data in aqueous ethanol. Migration of the phenyl group in the ketone product resulting from the *trans*-triflate **5** is nearly 50% and substantial, perhaps even approaching 50% if correction could be made for the deuterium isotope effect,[12] in the allene product. In any event, use of the combined data in Tables II and III allows calculation of 94% *as a lower limit* to phenyl participation, based upon the rearranged products, in the solvolysis of the trans isomer **5** in 60% aqueous ethanol. This is in excellent agreement with the 95% rearrangement predicted from the observed trans:cis rate ratio of 20 according to the Schleyer–Lancelot method,[13] assuming that the entire rate factor of 20 is due to anchimeric assistance by phenyl participation. Similarly, assuming that the entire experimentally observed trans:cis rate ratio of 62 in TFE is due to anchimeric assistance, this would require a product stereospecificity of 98.4%[13] in good agreement with the experimentally observed value of 98.3% calculated[14] from the data in Tables II and III.

Scheme I. Mechanism of Solvolysis of Vinyl Triflates **4** and **5**



Reisolation of partially solvolyzed **4a** and **5a** indicates that there is no cis–trans interconversion in the starting triflates[15] in either 60% EtOH or TFE and hence the partial rearrangement observed in the geometrically unfavorable cis isomer is real. However, reisolation and nmr examination of partially solvolized **5b** indicated the presence of some **5c** (but again no **4b** and **4c**) suggesting that the first formed intermediate must be an intimate ion pair **7b** capable of undergoing internal return. Interestingly, no such deuterium scrambling was observed in reisolated partially solvolyzed *cis*-triflate **4b**.

These results are best summarized and rationalized by the mechanism outlined in Scheme I. The *cis*-triflate **4** is preferentially ionized to the open vinyl cation **7a**. Ion pair **7a**, where the side of the molecule from which the triflate group is departing and hence shielded somewhat from solvent attack resulting in inverted product, is consistent with the large trans:cis vinyl ether ratio observed[16] in TFE. Similar inversion has been observed in the solvolysis[17b,20] of other alkyl-substituted stereoisomeric vinyl triflates. Besides solvent capture, ion pair **7a** may also lose a proton to give the observed allene. However, as the triflate gegenion in ion pair **7a** moves away and the initial unfavorable cis stereochemistry is lost, ion pair **7a** is capable of converting to the more stable bridged ion **7c** as demanded by the rearranged products observed in the solvolysis of **4b** and **4c** in 60% aqueous ethanol. The faster rate of reaction, the difference in product formation, and particularly the product stereochemistry[21] in the solvolysis of the trans isomer **5** indicate that it reacts predominantly, if not exclusively, *via* participation and bridged vinyl cation **7b**. Further evidence for these mechanisms is provided by the kinetic deuterium isotope effects in the solvolysis of **4** and **5** detailed in the accompanying communication.[22] Molecular orbital arguments by Hoffmann and coworkers[23] indicate that spiroarenes or bridged ions of the type **7b** are stable. Ion **7c** is the unsaturated vinyl cation analog, or a vinylidene phenonium ion, of the well-known[24] ethylene phenonium ion. Ion **7c** is also related to the sulfur-bridged cyclic thiirenium analog

(12) It is difficult to determine the exact deuterium isotope effect in the elimination step leading to the allene product. If it is a primary isotope effect and manifests itself substantially in the transition state leading to allene formation this could result in less than 50% rearranged product even if participation should be 100%.

(13) P. v. R. Schleyer and C. J. Lancelot, *J. Amer. Chem. Soc.*, **91**, 4297 (1969).

(14) This is true assuming that the 6.7% of allene observed in TFE consists of at least as much rearranged product (41%) as the allene observed in 60% EtOH.

(15) No formation or buildup of the much slower reacting cis isomer was observed at any stage of the reaction in the solvolysis of the trans isomer (limit of detection ~1%). Isomerization of the cis starting triflate to the trans isomer could of course not have been detected due to the much faster reaction of the latter. However, such isomerization seems equally unlikely under the reaction conditions employed.

(16) Other possibilities accounting for the high inversion may be significant amounts of backside S_N2 displacement. However, such S_N2 displacements are unlikely in vinyl systems.[17] Another possibility might be formation of an open free linear vinyl cation and a "natural" large preference for trans solvent capture. As linear vinyl cations that have two different β substituents possess diastereotopic faces[16] they *must* capture solvent at different rates. However, steric arguments and use of A values (C_6H_5 = 3.0, CH_3 = 1.7, $CH_3CH_2O \cong CF_3CH_2O$ = 0.9)[19] would predict a large preference for cis solvent capture, contrary to the experimental results.

(17) (a) D. R. Kelsey and R. G. Bergman, *J. Amer. Chem. Soc.*, **93**, 1953 (1971); (b) R. H. Summerville and P. v. R. Schleyer, *ibid.*, **94**, 3629 (1972).

(18) For discussion of stereoisomeric relationship, see: K. Mislow, "Introduction to Stereochemistry," W. A. Benjamin, New York, N. Y., 1965; K. Mislow and M. Raban, *Top. Stereochem.*, **1**, 1 (1967).

(19) J. A. Hirsch, *Top. Stereochem.*, **1**, 199 (1967).

(20) T. C. Clarke, D. R. Kelsey, and R. G. Bergman, *J. Amer. Chem. Soc.*, **94**, 3626 (1972); R. H. Summerville and P. v. R. Schleyer, *ibid.*, in press.

(21) Both an open ion pair or a linear free vinyl cation as well as backside S_N2 displacement would demand a much larger amount of cis product in TFE, which is contrary to observation.

(22) P. J. Stang and T. E. Dueber, *J. Amer. Chem. Soc.*, **95**, 2686 (1973).

(23) R. Hoffmann, A. Inamura, and G. D. Zeiss, *J. Amer. Chem. Soc.*, **89**, 5215 (1967).

(24) *Inter alia:* H. C. Brown and C. J. Kim, *J. Amer. Chem. Soc.*, **93**, 5765 (1971); J. A. Thomson and D. J. Cram, *ibid.*, **91**, 1778 (1969); P. v. R. Schleyer, *et al.*, *ibid.*, **91**, 4291, 4294, 4296, 4297 (1969); C. J. Lancelot, D. J. Cram, and P. v. R. Schleyer, "Carbonium Ions," Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1972, and references therein.

observed by Modena and coworkers[25] in the solvolysis of various β-arylthiovinylsulfonates.

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(25) *Inter alia:* G. Modena, *et al.*, *Chem. Commun.*, 1363, 1676 (1968); *Tetrahedron Lett.*, 4039 (1968); *J. Chem. Soc. C*, 2617, 2621, 2625 (1970); *J. Chem. Soc. B*, 374, 381, 1569, 1700 (1971); *Chem. Commun.*, 1520 (1969); 1325 (1971); *J. Chem. Soc., Chem. Commun.*, 8 (1972).

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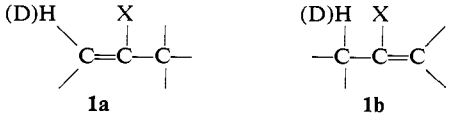
Secondary Kinetic Deuterium Isotope Effects in the Solvolysis of Vinyl Triflates. Further Evidence for a Vinylidene Phenonium Ion[1]

Sir:

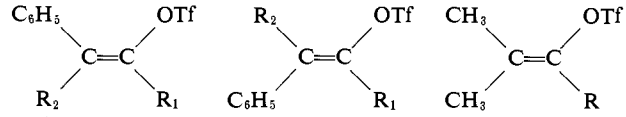
Deuterium isotope effects have been extensively employed in organic mechanistic studies,[2] particularly in the area of solvolytic displacement reactions. Similar to the deuterium isotope effects observed in normal carbonium ions, there may be several kinds of secondary deuterium isotope effects, α and β, in the solvolytic generation of vinyl cations. Observation of an α-deuterium isotope effect in a vinyl cation would require the formation of a highly energetic "primary" vinyl cation that has so far not been possible. On the other hand β-deuterium isotope effects should be readily observable. Indeed, in vinyl cations, there may be two different kinds of β-deuterium isotope effects: one where the isotopic substitution is β to the leaving group on an unsaturated carbon **1a**, and one where it is β but on an adjacent saturated carbon as in **1b**.[3] A number of



1a **1b**

examples of the former have recently been reported,[4,5] but to date no examples of the latter have been observed. In this communication we wish to report a β-deuterium isotope effect of the second kind as well as the first example of a kinetic γ-deuterium isotope effect in a vinyl cation.

The systems investigated are the *cis*- and *trans*-3-phenyl-2-buten-2-yl triflates **2** and **3** and the 3-methyl-2-buten-2-yl triflate **4**. Substrates **2** and **3** were prepared and isolated as described in the preceding communication,[1a] and **4** was prepared in a similar manner from 3-methyl-2-butanone. Rates were measured in 60% aqueous ethanol buffered with pyridine and are averages of three–six determinations. The results are summarized in Table I.



2a, $R_1 = R_2 = CH_3$; **b**, $R_1 = CD_3$; $R_2 = CH_3$; **c**, $R_1 = CH_3$; $R_2 = CD_3$ — **3a**, $R_1 = R_2 = CH_3$; **b**, $R_1 = CD_3$; $R_2 = CH_3$; **c**, $R_1 = CH_3$; $R_2 = CD_3$ — **4a**, $R = CH_3$; **b**, $R = CD_3$

Table I. Rates and Isotope Effects in the Solvolysis of Vinyl Triflates **2**, **3**, and **4**

Compd	Temp, °C	k, sec^{-1} [a]	k_H/k_D [b]
2a	99.81	$(9.30 \pm 0.24) \times 10^{-5}$	
2b	99.81	$(6.35 \pm 0.09) \times 10^{-5}$	1.47 ± 0.06
2c	99.81	$(1.03 \pm 0.02) \times 10^{-4}$	0.90 ± 0.04
3a	99.86	$(1.58 \pm 0.01) \times 10^{-3}$	
3b	99.86	$(1.37 \pm 0.01) \times 10^{-3}$	1.16 ± 0.02
3c	99.86	$(1.52 \pm 0.02) \times 10^{-3}$	1.04 ± 0.02
4a	74.96	$(1.30 \pm 0.02) \times 10^{-4}$	
4b	74.96	$(9.12 \pm 0.04) \times 10^{-5}$	1.46 ± 0.04 [c]

[a] Determined conductometrically, 0.6 μl/10 ml. [b] Uncorrected for small amounts of residual H's (4–9%) and for the scrambling observed in the trans substrates.[1] [c] Corrected for 8% H.

Two salient features emerge from the data in Table I. The β-deuterium isotope effect (α-CD_3 group) in the cis isomer **2b** is very much larger, $k_H/k_D = 1.47$, than for the corresponding trans isomer **3b** with $k_H/k_D = 1.16$. Control experiments[6] indicate that this difference is real and that the higher value in the case of the cis isomer is not due to a contribution from a primary isotope effect due to allene formation in the rate-determining step. The larger magnitude of k_H/k_D in **2b** is consistent with the cis isomer **2** ionizing to an essentially open linear vinyl cation, or ion pair,[1a] **5a**, and a greater charge concentration in the α position of the cis isomer in the transition state leading to **5a**. In contrast, there is considerable charge delocalization into the phenyl ring (with a concomitant reduction in the α position) and hence a lower isotope effect in the trans isomer **3** due to bridging in **5b**. Secondly, in the cis isomer **2c** the γ-deuterium isotope effect (β-CD_3 group) is inverse. Since deuterium is known to be electron donating relative to hydrogen, γ-deuterium isotope effects in normal trisubstituted carbonium ions are inverse[2] although

(1) (a) Paper VIII in a series on the preparation and solvolysis of vinyl triflates. Paper VII: P. J. Stang and T. E. Dueber, *J. Amer. Chem. Soc.*, **95**, 2683 (1973). (b) Presented at the 164th National Meeting of the American Chemical Society, New York, N. Y., Sept 1972.

(2) For reviews see: C. J. Collins and N. S. Bowman, Ed., "Isotope Effects in Chemical Reactions," Van Nostrand Reinhold Co., New York, N. Y., 1970; P. Laszlo and Z. Welvart, *Bull. Soc. Chim. Fr.*, 2412 (1966); E. R. Thornton, *Annu. Rev. Phys. Chem.*, **17**, 349 (1966); E. A. Halevi, *Progr. Phys. Org. Chem.*, **1**, 109 (1963); A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill, New York, N. Y., 1962; F. W. Westheimer, *Chem. Rev.*, **61**, 265 (1961); L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960; K. B. Wiberg, *Chem. Rev.*, **55**, 713 (1955).

(3) (a) This distinction may be extended to γ- as well as δ-deuterium isotope effects as in (D)HCC=C(X)C- and >C=C(X)CCH(D). (b) In the former case, *i.e.*, **1a**, a further distinction can be made on the basis of stereochemistry, depending on whether the deuterium is cis or trans to the leaving group.

(4) (a) D. S. Noyce and M. D. Schiavelli, *J. Amer. Chem. Soc.*, 90, 1023 (1968); (b) P. J. Stang and R. Summerville, *ibid.*, **91**, 4600 (1969); (c) W. M. Jones and D. D. Maness, *ibid.*, 92, 5457 (1970); (d) R. J. Hargrove, T. E. Dueber, and P. J. Stang, *Chem. Commun.*, 1614 (1970).

(5) P. J. Stang, *Progr. Phys. Org. Chem.*, **10**, 276 (1973).

(6) Vinyl triflate **2a** was found to be stable, with no trace of allene formation, in decane and in THF in the presence of pyridine or triethylamine at 100 and 130°, making the incursion of an E2 elimination along with the rate-determining formation of the intermediate vinyl cation unlikely.