

## Deuterium Isotope Effects in the Solvolytic Reactivity of Simple Alkylvinyl Trifluoromethanesulphonates<sup>1</sup>

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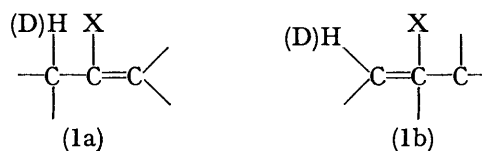
The kinetic as well as product deuterium isotope effects have been measured in the solvolysis of 1-trideuterio-methyl-2-methylprop-1-enyl (2b), *cis*- (3b), and *trans*-2-deuterio-1-methylprop-1-enyl (4b) trifluoromethanesulphonates as well as the 3,3,3-trideuterio-1-methyl-2-trideuteriomethylprop-1-enyl ester (2c). At 75° in aqueous 60% ethanol for (2b)  $k_H/k_D = 1.54$ , for (3b) 1.25, for (4b) 2.01, and for (2c) 0.96. The significance of these results are discussed.

IN recent years extensive investigations have been carried out into the direct solvolytic generation of vinyl cations.<sup>2</sup> Indeed, although solvolyses of vinylic systems normally proceed at considerably slower rates than those of the corresponding saturated systems,<sup>2-4</sup> a number of mechanistic criteria such as solvent effects,<sup>5-7</sup> substituent effects,<sup>4-7</sup> stereochemistry,<sup>8-10</sup> and rearrangements<sup>11-13</sup> all point towards a similarity of behaviour between saturated and unsaturated cations. Despite this abundance of data on the solvolytic generation of vinyl cations, little work has been reported on deuterium isotope effects in such systems although such effects have been widely employed in organic mechanistic studies.<sup>14</sup>

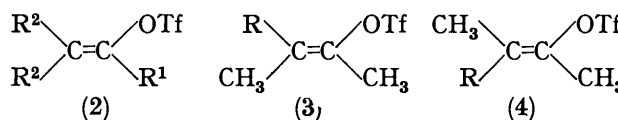
Similar to deuterium isotope effects observed in normal carbonium ions, there may be several kinds of secondary deuterium isotope effects such as  $\alpha$ ,  $\beta$ , and  $\gamma$  in the solvolytic generation of vinyl cations. Since an  $\alpha$ -deuterium isotope effect in a vinyl cation would require the formation of highly energetic 'primary' vinyl cations, hitherto not possible, such effects have not been observed except for a recent report<sup>15</sup> on  $\alpha$ -isotope effects in the solvolysis of the related halogenoallenes.

In vinyl cations there may be two different kinds of  $\beta$ -deuterium isotope effects, one where the isotopic substitution is  $\beta$  to the leaving group on an adjacent saturated carbon as in (1a) and one where it is on the neighbouring, unsaturated carbon as in (1b), a distinction that can be extended to  $\gamma$ - as well as  $\delta$ -deuterium

isotope effects. In the latter case (1b) a further distinction can be made on the basis of stereochemistry, depending on whether the deuterium is *cis* or *trans* to the leaving group.



In this paper we report  $\beta$ -deuterium isotope effects of both kinds together with the effect of stereochemistry as well as a  $\gamma$ -deuterium effect in the solvolysis of simple alkylvinyl trifluoromethanesulphonates (triflates). The systems investigated are the 1,2-dimethylprop-1-enyl triflates (2) and the *cis*- (3) and *trans*-2-methylprop-1-enyl triflates (4).



a; R<sup>1</sup> = R<sup>2</sup> = CH<sub>3</sub>                      a; R = H                      a; R = H  
 b; R<sup>1</sup> = CD<sub>3</sub>, R<sup>2</sup> = CH<sub>3</sub>                b; R = D                      b; R = D  
 c; R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = CD<sub>3</sub>

### RESULTS AND DISCUSSION

Vinyl triflates (2) were prepared from the corresponding ketones (5) and the anhydride of trifluoromethanesulphonic acid according to literature procedures.<sup>16</sup>

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<sup>14</sup> For reviews see (a) K. B. Wiberg, *Chem. Rev.*, 1955, **55**, 713; (b) L. Melander, 'Isotope Effects on Reaction Rates,' Ronald Press, New York, 1960; (c) F. W. Westheimer, *Chem. Rev.*, 1961, **81**, 265; (d) A. Streitwieser, jun., 'Solvolytic Displacement Reactions,' McGraw-Hill, New York, 1962; (e) E. A. Halevi, *Progr. Phys. Org. Chem.*, 1963, **1**, 109; (f) E. F. Thornton, *Ann. Rev. Phys. Chem.*, 1966, **17**, 349; (g) P. Laszlo and Z. Welvert, *Bull. Soc. chim. France*, 1966, 2412; (h) C. J. Collins and N. S. Bowman, 'Isotope Effects in Chemical Reactions,' Van Nostrand Reinhold, New York, 1970.

<sup>15</sup> M. D. Schiavelli and D. E. Ellis, *J. Amer. Chem. Soc.*, 1973, **95**, 7916.

<sup>16</sup> 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. Internat. Edn.*, 1970, **9**, 521; P. J. Stang and T. E. Dueber, *Org. Synth.*, 1974, **54**, in the press.

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<sup>5</sup> G. Modena, U. Tonellato, and F. Naso, *Chem. Comm.*, 1968, 1363; G. Modena and U. Tonellato, *J. Chem. Soc. (B)*, 1971, 374.

<sup>6</sup> C. A. Grob and G. Cseh, *Helv. Chim. Acta*, 1964, **47**, 194.

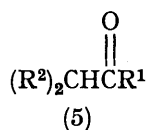
<sup>7</sup> R. H. Summerville, C. A. Senkler, P. v. R. Schleyer, T. E. Dueber, and P. J. Stang, *J. Amer. Chem. Soc.*, 1974, **96**, 1100.

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<sup>10</sup> Z. Rappoport and Y. Apeloig, *J. Amer. Chem. Soc.*, 1969, **91**, 6734.

Ketone (5b) was prepared by repeated exchange of the enolizable hydrogens of (5a) with D<sub>2</sub>O and NaOD.



- a; R<sup>1</sup> = R<sup>2</sup> = CH<sub>3</sub>  
b; R<sup>1</sup> = CD<sub>3</sub>, R<sup>2</sup> = CH<sub>3</sub>  
c; R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = CD<sub>3</sub>

Ketone (5c) was prepared from hexadeuterioacetone according to the Scheme. Triflates (3) and (4) were prepared<sup>1a</sup> from but-2-yne and CF<sub>3</sub>SO<sub>3</sub>H, and the deuterio-isomers by electrophilic addition of CF<sub>3</sub>SO<sub>3</sub>D; the mixture of *cis*- and *trans*-isomers was separated by g.l.c.

Rates were measured conductometrically in aqueous 60% ethanol and are averages of 2–6 determinations. The results are summarized in Table 1. Product studies

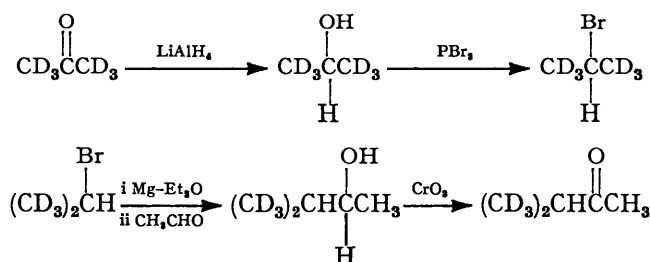
TABLE 1

Rates of reaction of vinyl triflates (2)–(4) in 60% EtOH

Compound	Temp. (°C)	k/s <sup>-1</sup>	ΔH <sup>‡</sup> /kcal mol <sup>-1</sup>	ΔS <sup>‡</sup> /cal mol <sup>-1</sup> K <sup>-1</sup>	
(2a)	25.0 *	2.30 × 10 <sup>-7</sup>	25.7	-2.8	
	65.01	(4.39 ± 0.041) × 10 <sup>-5</sup>			
	74.96	(1.26 ± 0.016) × 10 <sup>-4</sup>			
	85.04	(4.06 ± 0.10) × 10 <sup>-4</sup>			
	99.96	(1.76 ± 0.025) × 10 <sup>-3</sup>			
(2b)	119.99	(9.98 ± 0.023) × 10 <sup>-3</sup>	26.3	-1.7	
	25.0 *	1.34 × 10 <sup>-7</sup>			
	74.96	(9.09 ± 0.075) × 10 <sup>-5</sup>			
	99.84	(1.22 ± 0.020) × 10 <sup>-3</sup>			
	(2c)	25.0 *			2.67 × 10 <sup>-7</sup>
65.01		(4.51 ± 0.011) × 10 <sup>-5</sup>			
75.19		(1.43 ± 0.010) × 10 <sup>-4</sup>			
85.04		(4.18 ± 0.16) × 10 <sup>-4</sup>			
99.96		(1.69 ± 0.036) × 10 <sup>-3</sup>			
(3a)	199.99	(9.87 ± 0.016) × 10 <sup>-3</sup>	26.4	-1.5	
	25.0 *	1.16 × 10 <sup>-7</sup>			
	74.96	(8.13 ± 0.038) × 10 <sup>-5</sup>			
	99.92	(1.11 ± 0.010) × 10 <sup>-3</sup>			
	(3b)	74.96			(6.61 ± 0.044) × 10 <sup>-3</sup>
(4a)		25.0 *	5.15 × 10 <sup>-8</sup>		
		53.05	(1.97 ± 0.02) × 10 <sup>-4</sup>		
(4b)	74.96	(2.26 ± 0.02) × 10 <sup>-3</sup>			
	74.96	(1.26 ± 0.015) × 10 <sup>-3</sup>			

\* Extrapolated.

were carried out under similar conditions in 60% aqueous ethanol at 75° both buffered and unbuffered with pyridine. The observed products in all instances



SCHEME. Preparation of deuterio-ketone (5c).

are those expected from a vinyl cation intermediate<sup>2</sup> and are summarized in Table 2.

The ratios for the protio- and deuterio-compounds give a direct measure of the kinetic deuterium isotope effect and are summarized in Table 3. Similarly for compound (2) 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. For compound (3) the picture is

TABLE 2

Products of reaction of triflates (2)–(4) in 60% EtOH at 75° \*

Reactant	R <sup>1</sup> R <sup>2</sup> CHCR <sup>3</sup>			Yield (%)	Yield (%)	CH <sub>3</sub> C=CCH <sub>3</sub>			Yield (%)
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>			R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	
(2a) *	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	51.2		CH <sub>3</sub>	CH <sub>3</sub>	H	48.8
(2a)	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	54.2		CH <sub>3</sub>	CH <sub>3</sub>	H	45.8
(2b) †	CH <sub>3</sub>	CH <sub>3</sub>	CD <sub>3</sub>	65.5		CH <sub>3</sub>	CH <sub>3</sub>	D	34.5
(2b)	CH <sub>3</sub>	CH <sub>3</sub>	CD <sub>3</sub>	70.6		CH <sub>3</sub>	CH <sub>3</sub>	D	29.4
(2c)	CD <sub>3</sub>	CD <sub>3</sub>	CH <sub>3</sub>	52.7		CD <sub>3</sub>	CD <sub>3</sub>	H	47.3
(3a) †	H	CH <sub>3</sub>	CH <sub>3</sub>	27.1	58.2	CH <sub>3</sub>	H	H	14.7
(3a)	H	CH <sub>3</sub>	CH <sub>3</sub>	26.9	53.7	CH <sub>3</sub>	H	H	19.3
(3b) †	D	CH <sub>3</sub>	CH <sub>3</sub>	29.9	53.3	CH <sub>3</sub>	D	H	16.9

\* Limits of precision ±1.0%. † Buffered with pyridine.

TABLE 3

Deuterium isotope effects for triflates (2)–(4) in 60% EtOH at 75°

Compound	k <sub>H</sub> /k <sub>D</sub> *	ΔΔF <sup>‡</sup> /cal mol <sup>-1</sup> for deuterium atom	Product effect k <sub>H</sub> /k <sub>D</sub> *
(2b)	1.54	100	1.95
(2c)	0.86 (25°)	15	
(2c)	0.96 (75°)	5	1.07
(2c)	1.01 (120°)		
(3b)	1.25	154	1.26
(4b)	2.01	483	

\* Corrected to 100% D content, see Experimental section.

somewhat more complicated as there are three products with a potential primary isotope effect in acetylene formation and a secondary effect upon the formation of ketone and allene. If it is assumed that the secondary effect is negligible in comparison to the primary effect then the ratio of acetylene to the sum of ketone plus allene for the protio-compound (3a) over the same ratio for the deuterio-compound (3b) at least gives an indication of the isotope effect in product formation. These results are also summarized in Table 3. As the products were found to be more stable under buffered conditions and as the ratios of products were not much affected by buffering, only the buffered product isotope effects are reported in Table 3.

A number of interesting facts and trends emerge from these data. Although a direct comparison between our vinyl system and the analogous saturated substrate is not possible as no data exists in the literature on isotope effects in the 1-methylpropyl system, a comparison with the 1-methylethyl system is possible. The maximum

$\beta$ -deuterium isotope effect observed<sup>17</sup> in this system is  $k_H/k_D = 2.12$  for the tosylate at 25° in  $\text{CF}_3\text{CO}_2\text{H}$ , corresponding to a  $\Delta\Delta F^\ddagger$  of 75 cal mol<sup>-1</sup> per deuterium, with lower values of  $k_H/k_D = 1.2$  in aqueous ethanol. Assuming that under these conditions both solvolyses are limiting  $S_N1$  processes, which seems very likely, and neglecting differences due to leaving group, solvent, and temperature upon the isotope effect, which is not unreasonable in limiting cases,<sup>14</sup> this is some 25% less than the corresponding  $\beta$ -deuterium isotope effect in the vinyl substrate (2b). A higher  $\beta$ -deuterium isotope effect per deuterium atom in vinyl systems as compared to the analogous saturated systems is in line with the greater need of stabilization by hyperconjugation of a vinyl cation as compared with that of a normal carbonium ion. Such extra need for stabilization by a vinyl cation manifests itself as well by the greater stabilizing effect of  $\alpha$ - as well as  $\beta$ -methyl substitution in vinyl systems as compared to saturated carbonium ions as observed experimentally from appropriate solvolyses data<sup>7</sup> and *ab initio* calculations.<sup>18</sup>

The  $\gamma$ -deuterium isotope effects seem to be similarly larger for a vinyl system with  $k_H/k_D = 0.86$  for (2c) at 25° in 60% EtOH compared with  $k_H/k_D = 0.975$  for 2-chloro-2-methyl-4,4,4-trideuteriobutane also at 25° but in 80% EtOH.<sup>19</sup> The direction of this effect is in agreement with the normal inductive electron donating ability of deuterium as determined by pK measurements<sup>20</sup> for  $\text{CD}_3\text{CO}_2\text{H}$  relative to  $\text{CH}_3\text{CO}_2\text{H}$ .

As the data in Tables 1 and 3 show, the  $\gamma$ -deuterium isotope effect for (2c) shows a strong temperature dependence and in fact goes from an inverse effect of 0.96 at 75° to a normal value of 1.01 at 120°. Although this variation may be within the limits of precision of our data, it may also be real and represent an isokinetic effect<sup>21</sup> with a calculated isokinetic temperature of ca. 85°. Unfortunately, experimental conditions do not allow rate measurements at higher temperatures and hence a further check on the crossover.

A number of interesting observations can also be made concerning the isotope effects within the differing vinylic substrates. If it is assumed that the triflates (3) as well as (2) proceed through a similar linear vinyl cation  $\text{RCH}_2\text{C}^+\text{CCH}_3$  then as the data in Table 3 show the average reduction in free energy of activation per deuterium ( $\Delta\Delta F^\ddagger$ ) is some 55% greater for  $\beta$ -isotopic substitution on the double bond as in (1b) than for  $\beta$ -isotopic substitution on an adjacent saturated  $\alpha$ -carbon such as (1a). This confirms the strong dependence of  $\beta$ -deuterium isotope effects upon the dihedral angle

between the isotopically substituted C-H bond and the developing empty  $p$  orbital of the carbonium ion.<sup>22</sup> Indeed Shiner and his co-workers<sup>22</sup> have shown that the  $\beta$ -deuterium isotope effect is at a maximum when the dihedral angle is 0° and becomes inverse with a dihedral angle of 90°. In the cation resulting from (3) the  $\beta$ -hydrogen on the double bond is rigidly held in the same plane as the empty  $p$  orbital by the double bond of the vinyl cation whereas in the ion resulting from (2) free rotation is still allowed around the single bond  $\text{CH}_3\text{-C}^+\text{=C}$  resulting in a H-C dihedral angle of 30° with the  $p$  orbital, and hence less hyperconjugative overlap and a lower isotope effect. Furthermore, overlap is undoubtedly more effective across the shorter C=C double bond in (1b) than across the single bond in (1a).

A further and even more interesting manifestation of the strong hyperconjugative interaction and its dependence upon dihedral angle as it affects  $\beta$ -deuterium isotope effects in solvolyses is exhibited by the stereochemical effects in (3b) and (4b). The isotope effect of  $k_H/k_D = 2.01$  for (4b) is very much larger than the corresponding effect (1.25) for the *cis*-isomer (3b). A similarly large difference in *trans*- and *cis*-isotope effects of  $k_H/k_D = 1.57$  for *E*-2-deuterio-1-phenylvinyl fluorosulphonate and 1.10 for the corresponding *Z*-isomer were observed by Maness and Turrentine<sup>23</sup> in the acetolysis of these substrates relative to the parent protio-compound. These effects clearly show the importance of a *trans*-periplanar arrangement and further suggest that the transition state for ionization of vinyl substrates may be bent with the electron deficient orbital more strongly interacting with the *trans*-substituent. This spread in  $\beta$ -deuterium isotope effects as a function of stereochemistry is mirrored by a similar spread in  $\beta$ -substituent effects in solvolysis as a function of stereochemistry.<sup>7</sup> The effect of a  $\beta$ -substituent *trans* to the leaving group upon the solvolysis rate is almost as large as the effect of substituents on the  $\alpha$ -carbon despite the extra bond between the substituent group and the reaction centre.<sup>7</sup> Furthermore, similar large *trans*-effects have recently been observed in saturated systems.<sup>24</sup>

The product isotope effects summarized in Table 3 are equally instructive. In all substrates the product deuterium isotope effects closely parallel the kinetic deuterium isotope effects. This is all the more interesting as the product isotope effects in (2b) and (3b) involve breaking of the isotopically substituted C-H(D) bond in the transition state and hence are primary isotope

<sup>17</sup> A. Streitwieser, jun., and A. Dafforn, *Tetrahedron Letters*, 1969, 1263.

<sup>18</sup> L. Radom, P. C. Hariharan, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1973, **95**, 6531.

<sup>19</sup> P. D. Armstrong, in ref 14b.

<sup>20</sup> A. Streitwieser, jun., and H. S. Klein, *J. Amer. Chem. Soc.*, 1963, **85**, 2759.

<sup>21</sup> J. E. Leffler, *J. Org. Chem.*, 1955, **20**, 1202; J. E. Leffler and E. J. Grunwald, 'Rates and Equilibria of Organic Reactions,' Wiley, New York, 1963, p. 324; P. C. Vogel and M. J. Stern, *J. Chem. Phys.*, 1971, **34**, 779.

<sup>22</sup> (a) V. J. Shiner, jun., B. L. Murr, and G. Heinemann, *J. Amer. Chem. Soc.*, 1963, **85**, 2413; (b) V. J. Shiner, jun., and J. S. Humphrey, jun., *ibid.*, 1963, **85**, 2416; (c) V. J. Shiner, jun., and J. G. Jewett, *ibid.*, 1964, **86**, 945; (d) G. J. Karabatsos, G. C. Sonnichsen, C. G. Papaioannou, S. E. Scheppele, and R. L. Shone, *ibid.*, 1967, **89**, 463; (e) V. J. Shiner, jun., W. E. Buddenbann, B. L. Murr, and G. Lamaty, *ibid.*, 1968, **90**, 418; (f) B. L. Murr and J. A. Conklin, *ibid.*, 1970, **92**, 3464.

<sup>23</sup> D. D. Maness and L. D. Turrentine, *Tetrahedron Letters*, 1973, 755.

<sup>24</sup> R. Hoffman, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, 1972, **94**, 6221; R. C. Bingham and P. v. R. Schleyer, *Tetrahedron Letters*, 1971, 23.

effects that should have much larger values with magnitudes<sup>14</sup> of the order of  $k_H/k_D = 3-9$ . Hence the low magnitude of the experimentally observed product isotope effects must mean that the transition state for product formation occurs early along the reaction pathway<sup>25</sup> and must resemble the reactant, *i.e.*, the intermediate vinyl cation. This in turn implies that the elimination of a  $\beta$ -proton from a vinyl cation and formation of either allene or acetylene must be a low energy process with a very small or no activation energy. This is perhaps not unreasonable considering that  $\beta$ -elimination must compete favourably with solvent collapse of the intermediate ion which is undoubtedly a low energy process.

In summary, secondary deuterium isotope effects in vinylic solvolyses are considerably larger than in analogous saturated systems. The  $\beta$ -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  $\beta$ -C-H bond and the developing empty  $p$  orbital than in normal carbonium ions. Finally product isotope effects indicate that the  $\beta$ -elimination of a proton from an intermediate vinyl cation is a very ready process with a very small (if any) activation energy.

#### EXPERIMENTAL

N.m.r. spectra were recorded on a Varian A-60 spectrometer using tetramethylsilane as an internal standard and i.r. spectra were obtained on a Beckman IR-5 spectrometer. G.l.c. was performed on a Varian Aerograph 90-P or series 1200 unit using the following columns: A, 0.125 in  $\times$  10 ft 10% QF-1 on 60-80 Chromosorb G; B, 0.125 in  $\times$  10 ft 10% Carbowax 20 M on 60-80 Chromosorb G; C, 0.375 in  $\times$  15 ft 15% SF-96 on 60-80 Chromosorb W. Mass spectra were obtained on an MS-30 mass spectrometer.

**Materials.**—Trifluoromethanesulphonic acid was purchased from 3M Co. and used without further purification. But-2-yne was obtained from Farchan Research Laboratories, 3-methylbutan-2-one was purchased from Eastman Kodak Co., and 99.9% hexadeuterioacetone was purchased from Stohler Isotope Chemicals.

**Synthesis of Vinyl Triflates (2).**—Triflates (2a-c) were prepared from the corresponding ketones (5a-c) according to the following general procedure. A solution of commercial (5a) (2.58 g, 0.030 mol) and anhydrous pyridine (2.78 g, 0.035 mol) in anhydrous carbon tetrachloride (10 ml) was cooled to  $-78^\circ$  in an Erlenmeyer flask stoppered with a rubber septum. To the cooled solution trifluoromethanesulphonic anhydride (9.72 g, 0.034 mol) (obtained<sup>16a,26</sup> by distilling the acid from  $P_2O_5$ ) was added over 2-3 min with a syringe. The resulting mixture from which a white solid separated initially, was allowed to warm to room temperature and stand for 24 h, turning dark green. The mixture was filtered and the solid washed with several portions of  $CCl_4$ , then dissolved in water, and extracted with  $CCl_4$  (2  $\times$  10 ml). The combined  $CCl_4$  solu-

tions were washed with water (5 ml) and dried ( $MgSO_4$ ). The solvent was distilled and the residue vacuum distilled, b.p.  $49-55^\circ$  at 12 mmHg, yielding product (3.74 g, 58%) consisting of 90% (2a) and 10% 2-methyl-1-methylenepropyl triflate. The desired isomer (2a) may be obtained by vacuum distillation through an efficient column or by preparative g.l.c. on column C,  $\nu_{max}$  (neat) 1700 (C=C), 1210, and 1140  $cm^{-1}$  ( $SO_2$ ),  $\delta$  ( $C_6H_6$ ) 1.82br (3H, s,  $CH_3$ ), 1.63br (3H, s,  $CH_3$ ), and 1.42br (3H, s,  $CH_3$ ),  $m/e$ , 218 ( $M^+$ , 58%), 69 (75), 57 (92), 43 (100), 41 (44), and 39 (25).

Ketone (5b) was obtained by repeated exchange of (5a) with  $D_2O$  in the presence of catalytic amounts of NaOD. Triflate (2b) had  $\delta$  ( $C_6H_6$ ) 1.64 (3H,  $CH_3$ ) and 1.40 (3H,  $CH_3$ ) and mass spectrometric analysis showed the presence of 86.3% deuterium. Triflate (2c) had  $\delta$  ( $C_6H_6$ ) 1.81 (3H,  $CH_3$ ), mass spectrometric analysis showing 98.0% deuterium.

**Ketone (5c).**—To an anhydrous ether solution of  $LiAlH_4$  (4.94 g, 0.13 mol) [ $^2H_6$ ]acetone (25.6 g, 0.40 mol) was added slowly at  $-65^\circ$ . After 4 h at  $-65^\circ$  the solution was allowed to warm slowly to room temperature and  $H_2O$  (21 ml) added. The precipitate was filtered off and washed with ether. The combined ether solutions were dried and the ether distilled through a 16 in jacketed column packed with glass helices. The residue was distilled, b.p.  $76.5-77.5^\circ$  yielding 97% pure hexadeuteriopropen-2-ol (21 g, 80%),  $\nu_{max}$  (neat) 3267 (OH) and 2207  $cm^{-1}$  (CD),  $\delta$  (neat) 4.90 (1H, s, OH) and 3.8br (1H, d, CH).

To the above alcohol (20.5 g, 0.31 mol) at  $-65^\circ$  was added  $PBr_3$  (33.9 g, 0.12 mol) and the solution was allowed to warm slowly to room temperature and then heated at  $40^\circ$  for 1 h. Distillation through a Vigreux column yielded hexadeuterioisopropyl bromide (22.2 g, 55%), b.p.  $20-21^\circ$  at 20 mmHg,  $\nu_{max}$  ( $CCl_4$ ) 2201 and 1016  $cm^{-1}$ ,  $\delta$  (neat) 4.1 (1H, m, CH). This bromide (22.2 g, 0.172 mol) in ether (80 ml) was added over 2 h to Mg turnings (5.0 g, 0.21 g-atom) in ether (25 ml). The solution was then cooled to  $-10^\circ$  and freshly distilled acetaldehyde (22.8 g, 0.58 mol) was slowly added. The complex was decomposed with dilute  $H_2SO_4$  and the ether layer was separated. The water layer was extracted with several portions of ether and the combined organic layers dried ( $MgSO_4$ ). The ether was carefully distilled through a 16 in column packed with glass helices. The residue was distilled yielding [ $^2H_6$ ]-3-methylbutan-2-ol, b.p.  $102-105^\circ$ ,  $\nu_{max}$  (neat) 3295 (OH) and 2202  $cm^{-1}$  (CD),  $\delta$  ( $CCl_4$ ) 3.85 (1H, s, OH), 3.38 (1H, quint, HCOH), 1.52br (1H, d, CH), and 1.05 (3H, d,  $CH_3$ ). This alcohol was oxidized to (5c) with aqueous chromic acid according to the procedure of Brown *et al.*<sup>27</sup> in 56% yield,  $\nu_{max}$  (neat) 2940 (CH), 2232 (CD), and 1710  $cm^{-1}$  (C=O),  $\delta$  (neat) 2.48br (1H, d, CH) and 2.01 (3H, s,  $CH_3$ ), containing 96.4% deuterium by mass spectroscopy.

**Vinyl Triflates (3) and (4).**—A solution of but-2-yne (8.0 g, 0.15 mol) in dry pentane (50 ml) was cooled to  $-20^\circ$  and stirred while  $CF_3SO_3D$  (7.8 g, 0.051 mol) [from  $(CF_3SO_2)_2O + D_2O$ ] in pentane (50 ml) was slowly added over 3 h. The mixture was allowed to warm to  $+20^\circ$ , then washed with unsaturated  $NaHCO_3$  solution (2  $\times$  5 ml). The pentane solution was dried ( $MgSO_4$ ) and the solvent distilled at atmospheric pressure. The residue was distilled giving an 80:20 mixture of (4b) and (3b) (5.2 g, 49%), b.p.  $39-40^\circ$  at 20 mmHg. The mixture was separated by

<sup>25</sup> W. T. Ford, *Accounts Chem. Res.*, 1973, **6**, 410; D. Cook, R. E. Hutchingson, J. K. MacLeod, and A. J. Parker, *J. Org. Chem.*, 1974, **39**, 534.

<sup>26</sup> J. Burdon, I. Farazmand, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 1957, 2574.

<sup>27</sup> H. C. Brown, C. P. Garg, and K. T. Lin, *J. Org. Chem.*, 1971, **36**, 387.

preparative g.l.c. on column C. Compound (3b) had  $\delta$  ( $\text{CCl}_4$ ) 2.17 (3H, m,  $\text{CH}_3$ ,  $^5J$  ca. 0.9 Hz) and 1.80 (3H, m,  $\text{CH}_3$ ,  $^5J$  ca. 0.9 Hz), with 89.8% deuterium by mass spectroscopy: (4b) had  $\delta$  ( $\text{CCl}_4$ ) 2.04 (3H, m,  $\text{CH}_3$ ,  $^5J$  ca. 1.4 Hz), 1.70 (3H, m,  $\text{CH}_3$ ,  $^5J$  ca. 1.4 Hz), and 5.30 (0.2H, m, CH), with 79.6% deuterium by mass spectroscopy. Triflates (3a) and (4a) were similarly prepared<sup>1a</sup> by addition of  $\text{CF}_3\text{SO}_3\text{H}$ .

*Kinetic Measurements.*—Rate studies were carried out conductometrically in aqueous 60% ethanol (v/v), unbuffered, with ca. 0.2  $\mu\text{l}$  substrate per 4.0 ml solvent in carefully controlled constant temperature baths. Ethanol was purified by treating commercial 99.5% ethanol with sodium metal, then ethyl phthalate, according to the method of Wiberg.<sup>28</sup> Excellent first-order rates were observed in all instances for over 5 half-lives. The rates were calculated by a non-linear, least-squares program (LSKIN-1)<sup>29</sup> and are the average of 2–6 determinations.

<sup>28</sup> K. B. Wiberg, 'Laboratory Technique in Organic Chemistry,' McGraw-Hill, New York, 1960.

*Product Studies.*—Product studies were carried out in all instances by means of internal standards and with authentic samples and analysed by g.l.c. on column A and B. Reactions were allowed to proceed for 3–4 half-lives and were carried out both in buffered (pyridine) and unbuffered aqueous 60% ethanol at 75°. Products were found to be stable under the reaction conditions in buffered media while minor changes in products were observed in unbuffered media.

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<sup>29</sup> D. F. DeTar and C. E. DeTar, 'Computer Programs in Chemistry,' Benjamin, New York, 1969.