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Solvolysis of 1-Pent-3-ynyl Triflate. Mechanism of the Homopropargyl Rearrangement[1]

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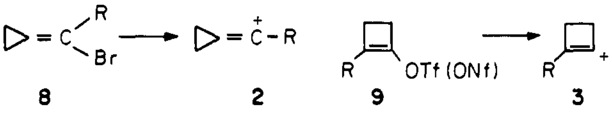
Abstract: 1-Pent-3-ynyl triflate (**1b**) was solvolyzed (25 °C, 24 h) in ethanol–water with 2,6-lutidine as the buffer. Products were formed predominantly (97–98.5%) through direct substitution (k_s processes) and elimination. As the water content increases, the yields of 2-methylcyclobutanone (**7b**) (formed through k_Δ processes) also increase from 0.2% (100% ethanol) to 2.8% (50% ethanol). 1-Pent-3-ynyl triflate was solvolyzed in anhydrous trifluoroethanol (25 °C, 24 h) in nine different experiments with nine different buffers. Sodium and calcium carbonate, 2,6-lutidine, pyridine, and quinoline all favored k_Δ processes (88–65%), whereas potassium carbonate, triethylamine, and sodium trifluoroethoxide suppressed the formation of rearranged products. The products of the solvolyses include: 2-methylcyclobutenyl trifluoroethyl ether (**5b**); cyclopropyl methyl ketone (**6b**); 2-methylcyclobutanone (**7b**); pent-1-en-3-yne (**13**); 1-pent-3-ynol (**15**); 2-methylcyclobutanone bis(trifluoroethyl) acetal (**16**), and 1-pent-3-ynyl trifluoroethyl ether (**17**). In 80% trifluoroethanol–20% water (sodium carbonate buffer) the yields of rearranged products (k_Δ) dropped to 46%—as expected for an increase in nucleophilicity of the solvent. A quantitative correlation exists between percent rearrangement of **1b** and nucleophilicity of the solvent, as demonstrated by use of the Winstein–Grunwald–Swain equation. 1-Pent-3-ynyl triflate was synthesized with carbon-14 in the 1 position (**1b**-*1*-^{14}C) and, separately, in the 3 position (**1b**-*3*-^{14}C). 1-Pent-3-ynyl triflate was also prepared doubly labeled both with carbon-14 and with deuterium (**1b**-*3*-^{14}C-*1,1*-d_2). Isotope effects were determined for all isotope position isomers. These are: $k/{}^*k = 1.048 \pm 0.003$ (**1b**-*1*-^{14}C); $k/{}^*k = 0.990 \pm 0.005$ (**1b**-*3*-^{14}C); and $^Hk/^Dk = 1.098 \pm 0.004$ (**1b**-*1,1*-d_2). In addition, **1b**-*1,1*-d_2 on solvolysis in trifluoroethanol–sodium carbonate yields 2-methylcyclobutanone (**7b**) containing equal fractions of **7b**-*3*-d_2 and **7b**-*4*-d_2. The tracer and isotope effect experiments confirm the mechanistic conclusions arrived at through product distribution studies and, in addition, offer strong evidence for significant anchimeric assistance during the k_Δ processes investigated.

Homoallylic participation leading to carbenium ion intermediates is a long-established[2] phenomenon, and double bonds even more remotely placed (than in homoallyl) from the site of bond scission are also known[2] to participate in the rate-determining step. In both cases participation can increase the solvolysis rate with respect to the rates of the corresponding saturated reactants.

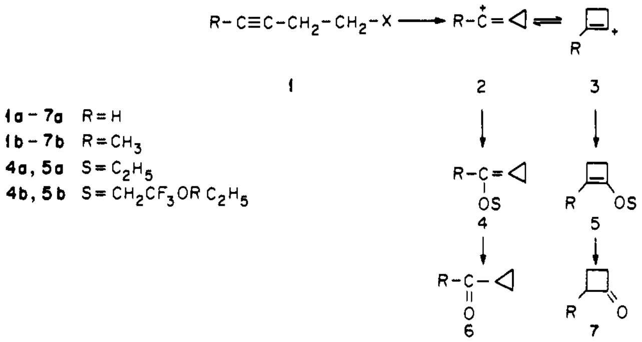
Participation by a triple bond was discovered[3] in 1965 during solvolysis of a homopropargyl tosylate, which resulted in rearranged products similar to those observed[2] during solvolysis of homoallyl derivatives. Solvolysis in appropriate solvents of compounds with structure **1** occurs with participation of the triple bond (k_Δ process) and leads to the cyclopropylidenemethyl (**2**) and the cyclobutenyl (**3**) cations (Scheme I). A second mechanism, addition of solvent to the triple bond of **1** followed by a rearrangement of the intermediate homoallyl compound, has been definitely excluded.[3]

The cyclopropylidenemethyl (**2**) and the cyclobutenyl (**3**) cations are intermediates in the solvolyses of the highly reactive cyclopropylidenemethyl bromides (**8**)[4] and the cyclobutenyl triflates and nonaflates (**9**).[5]



R= H, ALKYL, ARYL.

Scheme I



The stabilities of vinyl cations **2** and **3** have been documented experimentally,[2-4] and also theoretically,[6] for the parent cations **2a** and **3a**[7] through MO, ab inito, and MINDO/3 calculations. Cation **3a** was found to be significantly more stable than cation **2a**, which itself is stabilized by hyperconjugation. The energy difference between **3a** and **2a**, however, is greater than that between the methyl-substituted cations **2b** and **3b**. The calculations for **2a** and **3a** have been fully confirmed by collisional activation mass spectrometry, which revealed that both cations are stable species in the gas phase.[8] According to these[6-8] results, the homopropargyl cation **10** is much less stable than **2a** and **3a**.

$$H{-}C{\equiv}C{-}CH_2CH_2^+$$
10

Our earlier results on the homopropargyl rearrangement can be summarized briefly as follows:[9,10] homopropargyl derivatives

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Table I. Solvolysis of 1-Pent-3-ynyl Triflate (1b) in Ethanol/Water Mixtures[a]

solvent (ethanol-water) % ethanol	% yield of solvolysis products 13	7b	14	15
100	0, 5	0, 2	98	
80	5	1, 3	74	18
50	1	2, 8	50	46

[a] 25 °C, 1 day, buffer (B) 2,6-lutidine (1a:B:solvent = 1:2:80); direct gas chromatographic analysis; internal standard, *p*-xylene.

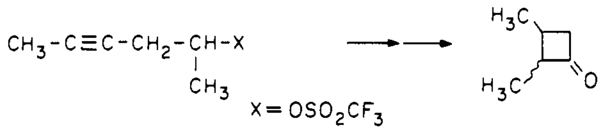
Table II. Solvolysis of 1-Pent-3-ynyl Triflate (1b) in TFE[a]

solvent, %	buffer	solvolysis products, % 13	5b	16	7b	6b	17	15
100	Na_2CO_3	1	83	3	2	<1	7	1
100	2,6-lutidine	<1	78	<1	1	<1	16	<1
80[b]	Na_2CO_3	2	26	1	19	1	44	3

[a] At 25 °C, 1 day, standard: benzene (1a:B:S = 1:2:40). [b] 20% H_2O.

of structure **1** rearrange quantitatively with formation of cyclopropyl ketones **6** or/and cyclobutanones **7** if the solvolysis reactions are carried out in solvents (e.g., formic acid, trifluoroacetic acid, aqueous TFE) of low nucleophilicity and high ionizing power to allow participation of the triple bond (k_Δ process) and to avoid direct substitution (k_s process). In solvents of high nucleophilicity (e.g., ethanol), the products are formed primarily through substitution without rearrangement.[9,10] The use of good leaving groups (tosylates, *p*-nitrobenzenesulfonates, and especially triflates) which are able to promote S_N1 reactions leads to high yields of rearranged products **6** and **7**. The ratio of the rearranged ketones **6** and **7** is dependent upon the substituent R in the homopropargyl compound **1**. If R = H or alkyl, the corresponding cyclobutanones **7** (R = H, alkyl) are the chief products; when R = aryl or cyclopropyl, the cyclopropyl ketones **6** (R = aryl, cyclopropyl) predominate. When R = aryl or cyclopropyl, products from cation **2** predominate as demonstrated in the solvolyses of alkyl, aryl, and cyclopropyl substituted cyclopropylidenemethyl (**8**)[4] and cyclobutenyl bromides (**9**).[5] The homopropargyl derivatives **1** (X = OTs, OTf), the cyclopropylidenemethyl (**8**), and cyclobutenyl compounds (**9**) all solvolyze under comparable conditions to yield similar product mixtures, indicating that in all cases the solvolysis reactions proceed via the same kinds of intermediates.

Secondary homopropargyl derivatives **11** also solvolyze with cyclization to yield mostly the corresponding cyclobutanones **12**.[9-11] The homopropargyl rearrangement is of preparative interest for the synthesis of cyclobutanone and substituted cyclobutanones. For example, the rearrangement of 1-but-3-ynyl triflate (**1a**) takes place[12] almost quantitatively in trifluoroacetic acid–sodium trifluoroacetate to produce cyclobutanone (**7a**) (Scheme I).



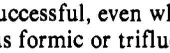
11 **12**

In this paper we present further evidence for the mechanism of the homopropargyl rearrangement. For this purpose the solvolyses of 1-pent-3-ynyl triflate (**1b**) were carried out in different solvent mixtures with a variety of buffers, and the effects on product distribution were determined. In addition carbon-14 and deuterium isotope effects were measured in order to study triple-bond participation in the carbenium ion forming process.[13]

In a future paper[14] we report on the rearrangement of aryl- and cyclopropyl-substituted homopropargyl compounds, thereby studying the effect of substituents in the 3 position on the identities and yields of the solvolysis products.

Results and Discussion

1-Pent-3-ynyl triflate (**1b**) was first solvolyzed in ethanol buffered with 2,6-lutidine containing different amounts of water. The product composition relative to the water concentration in ethanol is shown in Table I. Because of the low ionizing strength and high nucleophilicity of ethanol,[15] very little of the k_Δ product 2-methylcyclobutanone (**7b**) was formed (Table I); there was no evidence for the presence of either ethyl 2-methylcyclobutenyl ether (**5b**, S = C_2H_5) or the compounds **4b**, **5b** (S = C_2H_5), or **6**. The main solvolysis product is ethyl 1-pent-3-ynyl ether (**14**) formed by direct substitution. Increasing the water concentration and thereby increasing the ionizing strength of the solvent mixture leads to an increase in the yields of the cyclization products **7b** (Table I). Collapse of the vinyl cations **2** and **3** with the corresponding anions should produce the enols, enol ethers, or enol esters **4** and **5**, although all our efforts to isolate them have, until recently, been unsuccessful, even when the solvolyses were carried out in anhydrous formic or trifluoroacetic acids. Solvolysis of 1-pent-3-ynyl triflate (**1b**) in anhydrous trifluoroethanol (TFE), however, enabled us to isolate 2-methylcyclobutenyl trifluoroethyl ether (**5b**), along with minor amounts of other products (Table II), in yields of 78–83%.[16] Compound **5b** was isolated by preparative GC and identified through its ^1H NMR spectrum. For an additional structure proof, **5b** was treated for 5 min with 1 M H_2SO_4 at room temperature, after which it was converted quantitatively into 2-methylcyclobutanone (**7b**). Table II shows the product composition from the solvolysis of **1b** in absolute TFE and in 80% TFE using Na_2CO_3 and 2,6-lutidine as buffers.



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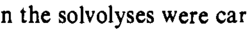

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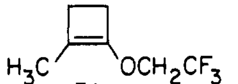

5b

As can be seen from Table II, trifluoroethanol, because of its low nucleophilicity,[17] is a suitable solvent for promoting the homopropargyl rearrangement, and leads to a high ratio of cyclized products. In 80% TFE the nucleophilicity of the solvent mixture is increased; this is accompanied by a decrease in the yield of cyclization product (k_Δ process) and an increase in the yields of the nonrearranged substitution products **17** and **15** (k_s processes). A small percentage of 2-methylcyclobutanone bis(trifluoroethyl) acetal (**16**) is also produced by the addition of TFE to the double bond of the enol ether **5b**. This was demonstrated by the formation of **16** upon treatment of **5b** with TFE at room temperature. Trifluoroethanol does not add to the triple bond of **15** nor is the enol ether **5b** formed from the acetal **16** under the conditions employed during the solvolyses.

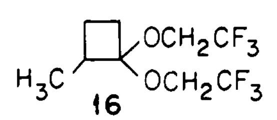

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Table III. Dependence of the Product Composition upon the Buffer Used in the Solvolysis of 1-Pent-3-ynyl Triflate (1b)[a]

expt		solvolysis products in %							
no.	buffer	**13**	**5b**	**16**	**7b**	**6b**	**17**	**15**	ΣF^b
1	Na_2CO_3	<1	83	3	2	<1	7	<1	88
2	$CaCO_3$			34	52		9		86
3	2,6-lutidine	<1	78	<1	1	<1	16	<1	79
4	pyridine	<1	84	<1	3		10	<1	87
5	quinoline	1	68	2	4		19	2	74
6	urea	<1		26	39	1	24	3	65
7	K_2CO_3	6	8		<1		80	6	8
8	TEA[c]	7	10	<1	<1	<1	81		10
9	$NaOCH_2CF_3$	5	10	<1	<1		81	3	10

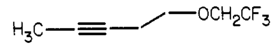
[a] In absolute TFE at 25 °C, 24 h, standard: benzene (**1b**:B:S = 1:2:40), 20-m glass capillary column, K20M, 140 °C. [b] ΣF = sum of the four-membered ring compounds 5b + 7a + 16. [c] Triethylamine.

Table IV. Percent Rearrangement (*R*) of 1-Pent-3-ynyl Triflate (1b) in Different Solvents[9,10,20]

solvent	*Y*	*N*	*R*
60% acetone	0.66	−0.41	1.5
50% MeOH	1.97	−0.18	4
100% TFE	1.80	−3.0/−3.8[a]	89
100% CF_3COOH	4.57	−5.56	99.99

[a] Both values are given in the literature.[20]

The ratios of the solvolysis products of **1b** in TFE were found to be strongly dependent upon the base used as the buffer. This is shown in Table III. With Na_2CO_3, $CaCO_3$, pyridine, 2,6-lutidine, quinoline, or urea as buffers, the reactions of **1b** take place predominatly with participation of the triple bond to form **5b**, **7b**, and a small amount of the acetal **16**. The sum ($\sum F$) of the yields of compounds with four-membered rings does not change drastically with these six buffers; $CaCO_3$ and urea appear to promote the addition of TFE to the double bond of **5b**, since they are associated (Table III) with high yields of **16** and no **5b** at all. Potassium carbonate and triethylamine (TEA), on the other hand, enhance the k_s processes at the expense of the k_Δ processes, since product **17** predominates (80–81%). Potassium carbonate reacts



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with TFE to form potassium trifluoroethylate.[18] The product yields (Table III) are similar when either K_2CO_3 (expt 7) or $NaOCH_2CF_3$ (expt 9) are buffers. It is interesting that the reaction with TEA (expt 8) closely resembles expt 7 and 9. Perhaps TEA itself reacts with trifluoroethanol to form triethylammonium trifluoroethylate.

Whereas the product composition of the TFE solvolysis of **1b** is not sensitive to the concentration of Na_2CO_3, 2,6-lutidine, or pyridine, an increasing TEA concentration in TFE leads to more elimination (formation of **13**, Table III) and more S_N2 substitution (formation of ether **17**). On the other hand, the percent of four-membered ring compounds ($\sum F$) decreases. Hence it follows that the percent rearrangement (*R*) to form four-membered, and to a lesser extent, three-membered ring compounds in the homopropargyl rearrangement is strongly dependent upon the nucleophilicity of the solvent. This is shown on a more quantitative basis in Table IV in which the percent of rearrangement (*R*) in different solvents and the known *Y* and *N* values derived from the Winstein–Grunwald–Swain equation (eq 1) are given.[19] The

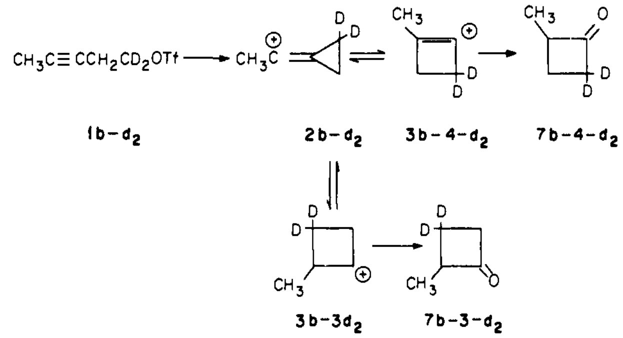
$$\log k/k_0 = mY + lN \qquad (1)$$

Table V. Percent Rearrangement (*R*) of 1-Pent-3-ynyl Triflate (1b)

solvent	*R*, % (calcd)	*R*, % (found)
100% EtOH	0.05	0.1–0.2
80% EtOH	0.4	1.4
50% EtOH	1.7	2.8
97% HFIP	99.7	96
100% TFE	84[a]	89
97% TFE	79	76
80% TFE	43	47

[a] $Y = -3.0$, with $Y = -3.8$ an *R* of 96% is calculated.

Scheme II



experimental data given in Table IV allow an estimation of the percent rearrangement (*R*) in other solvents.[21] The results are given in Table V. The calculated ratios of rearrangement are in very good agreement with the experimental values.

We turn now to the isotopic studies. First, the 50:50 distribution of deuterium in the methylcyclobutanone-d_2 (**7b**-d_2) (Scheme II) obtained on trifluoroethanolysis of **1b**-d_2 is additional evidence for the mechanism of the reaction as outlined in Schemes I and II, and demonstrates the necessity for the symmetrical intermediate **2b**. This result (Scheme II) means either that (1) cation **2b** is formed first and then rearranges to **3b**, or (2) if **3b** is formed directly from 1-pent-3-ynyl triflate (**1b**), the equilibrium **2b** ⇌ **3b** between the two vinyl cations must be complete before reaction with entering group takes place.

We may calculate the isotope effects for the trifluoroethanolyses of 1-pent-3-ynyl-*1*-^{14}C triflate (**1b**-*1*-^{14}C), 1-pent-3-ynyl-*3*-^{14}C (**1b**-*3*-^{14}C), and 1-pent-3-ynyl-*1*,*1*-d_2 triflate (**1b**-d_2) from the data in Table VI. (See Experimental Section.) The results are shown under the appropriate formulas.

$$CH_3C{\equiv}CCH_2\overset{*}{C}H_2OTf \qquad CH_3C{\equiv}\overset{*}{C}CH_2CH_2OTf \qquad CH_3C{\equiv}CCH_2CD_2OTf$$

$$\frac{k}{{}^{*}k} = 1.048 \pm 0.003 \qquad \frac{k}{{}^{*}k} = 0.990 \pm 0.005 \qquad \frac{{}^{H}k}{{}^{D}k} = 1.098 \pm 0.004$$

(per deuterium)

We shall consider first the two carbon-14 isotope effects. It is well known[22] that primary heavy atom isotope effects (^{14}C, ^{13}C) are large in S_N2 reactions, and very small in S_N1 reactions. The reason for small ^{14}C or ^{13}C isotope effects in S_N1 reactions is ascribed[22] to the effect on the double differences in zero-point energies between ground and transition states caused by those structural features which stabilize the cationic intermediate (and thus also stabilize the transition state which precedes it) and cause additional bonding to the carbon possessing the positive charge. When these factors are in balance with zero-point energy differences due to bond cleavage at the leaving group, the primary carbon isotope effect approaches unity. When these stabilizing factors offset those due to bond breaking, $^{12}k/^{14}k$ can be less than

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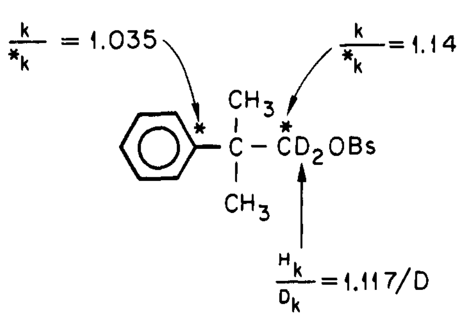

Figure 1. Isotope effects[26,29] in the solvolyses of neophyl esters.

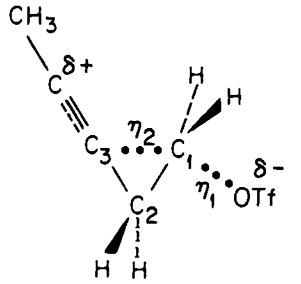

Figure 2. Presumed transition state for solvolysis of 1-pent-3-ynyl triflate (**1b**).

unity.[23] The value observed, $^{12}k/^{14}k = 1.048 \pm 0.003$, for the trifluoroethanolysis of **1b**-1-^{14}C is clearly consistent with an S_N2-like transition state, although lower than that reported ($^{12}k/^{14}k = 1.14$) for a similar case, in the trifluoroacetolysis of neophyl-1-^{14}C brosylate (see Figure 1). The β-^{14}C isotope effect ($^{12}k/^{14}k = 0.990 \pm 0.005$) in the trifluoroethanolysis of 1-pent-3-ynyl-3-^{14}C triflate is also much smaller than that shown in Figure 1. The significant, but relatively small, value of $^{12}k/^{14}k$ for **1b**-1-^{14}C can be explained by assuming that the transition state for trifluoroethanolysis of **1b**, portrayed in Figure 2, is unsymmetrical; that is to say, the bond orders, n_2 and n_1, of the developing and cleaving bonds, respectively, are not only unequal, but significantly different. Fry[24] and Sims[25] have calculated that maximum primary ^{14}C or ^{13}C isotope effects are observed when the transition states in S_N2 reactions are close to symmetrical ($n_2 = n_1$). This bell-shaped relation of primary isotope effect to bond order has been confirmed[26] experimentally by Yamataka and Ando. For either situation (a) $n_2 > n_1$ or (b) $n_2 < n_1$, $^{12}k/^{14}k$ should be reduced. Both values[27] of $^{12}k/^{14}k$ for neophyl brosylate, shown in Figure 1, are large, and the primary isotope effect is near the maximum, so we presume the S_N2-like transition state is symmetrical, or nearly so, which is equivalent to saying that $n_2 \simeq n_1$. Wilson[28] studied both the kinetics and the β-^{14}C isotope effects for para-substituted neophyl brosylates in which carbon-14 was present in the 1 position of the substituted benzene ring. The $(^{12}k/^{14}k)_\beta$ for *p*-methoxy hydrogen, and *p*-bromo were, respectively, 1.0061, 1.0306, and 1.0407. Shiner and Sieb[29] also studied para-substituent effects during neophyl solvolyses on α-deuterium isotope effects and concluded that electron-releasing substituents in the para position of the phenyl produces a more reactant-like transition state. The conclusions of both Wilson[28] and of Shiner and Sieb[29] assist in the interpretation of our own results. The very small $^{12}k/^{14}k$ (0.990 ± 0.005) for the solvolysis of 1-pent-3-ynyl triflate (**1b**-3-^{14}C) indicates a reactant-like transition state ($n_1 \gg n_2$), a lower activation energy than if n_2 and n_1 were more nearly equal, and considerable neighboring group participation[30] by the triple bond, but a participation which is obviously small by comparison with that exhibited by water as a solvent in the S_N2 process. We make no claim that the value 0.990 ± 0.005 is significantly different from unity; the important fact here is that the value is so much smaller than that reported[26,29] for the corresponding value which was observed during solvolysis of neophyl esters (Figure 1). The presumption that $n_1 \gg n_2$ also helps explain the relatively low ($^{12}k/^{14}k = 1.048 \pm 0.003$) primary carbon-14 isotope effect (compare with $^{12}k/^{14}k = 1.14$ for trifluoroacetolysis of neophyl-1-^{14}C brosylate, Figure 1).

We turn now to the trifluoroethanolysis ($^{H}k/^{D}k = 1.098 \pm 0.004$) of **1b**-$1,1$-$d_2$. α-Deuterium isotope effects should be at a maximum for S_N1 reactions and at a minimum for S_N2 reactions.[31] The reason for this is that $(^{H}k/^{D}k)_\alpha$ is due primarily to the differences in out-of-plane bending of hydrogen vs. deuterium in the ground and transition states. A more crowded transition state (S_N2) should, therefore, reduce $(^{H}k/^{D}k)_\alpha$. Although the transition state for trifluoroethanolysis of **1b** is S_N2-like, it is not a *linear* transition state (with respect to entering group, central carbon, and leaving group), but must be bent, somewhat as shown in Figure 2. Consequently the $(^{H}k/^{D}k)_\alpha$ should reflect the reduced crowding and be somewhat higher than expected for normal S_N2 reactions.[32] Shiner and Sieb[29] solvolyzed neophyl-$1,1$-d_2 mesylate, and the *p*-methoxy, *p*-methyl derivatives, as well as *m*-trifluoromethylneophyl-$1,1$-d_2 triflate in trifluoroethanol, and determined that $(^{H}k/^{D}k)_\alpha$ was between 1.099 and 1.134. The ethanolyses were in about the same range. Our value of $(^{H}{}_{k}/^{D}{}_{k})_\alpha = 1.098 \pm 0.003$ is consistent with these results, and these relatively high values for $(^{H}k/^{D}k)_\alpha$ may be ascribed in part to reduced crowding in the bent transition states.

Shiner and Sieb[29] rationalize their results with energy contour diagrams described by O'Ferrall[33] and Jencks.[34] They noted that an electron-attracting group in the para position in their neophyl mesylates, brosylates, and triflates increases the energy of the solvolytic intermediate, and "may increase $Ph\cdots C_\alpha$ formation more than it increases $C_\alpha\cdots O$ bond breakage." Para-electron-releasing groups, however, make the transition state more reactant-like ($n_1 \gg n_2$), which should decrease $^{12}k/^{14}k$ at both C-1 and C-3, and tend to increase $(^{H}k/^{D}k)_\alpha$. The latter situation is consistent with the isotope effects reported here for the various isotope position isomers of **1b**, namely, a reactant-like transition state coupled with considerable anchimeric assistance by the triple bond.

The kinetics of the solvolyses of **1a** and of some other homopropargyl triflates are the subject of a future paper.[14]

Experimental Section

Synthesis of 1-Pent-3-ynyl Triflate and Its Isotope Position Isomers. The unlabeled 1-pent-3-ynyl triflate (**1b**) was prepared from 1-pent-3-ynol by treatment with trifluoromethanesulfonic acid anhydride in methylene chloride in the presence of sodium carbonate.[35] The triflate was purified by distillation. **1-Pent-3-ynyl triflate (1b)**: ^1H NMR δ (ppm) 1.76 (t, 3 H, CH_3, $J = 2.5$ Hz), 2.45–2.85 (m, 2 H, $C-C-CH_2-$), 4.5 (t, 2 H, OCH_2-).

The general procedure used for the synthesis of isotope position isomers of 1-pent-3-ynol is as follows: To 50 mL of benzene there were added 10.6 g (0.0394 mol) of triphenylphosphine and 6.12 g (0.0394 mol) of ethyl bromoacetate. The mixture was stirred and allowed to stand overnight. The crystalline product was collected on a filter, washed with fresh benzene, and dried. It was then dissolved in water, decolorized with

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Norit, and treated with 10% sodium hydroxide solution. The resulting crystalline ethyl phosphoranylidene acetate was recrystallized from chloroform–ether–hexane mixture to give 6.5 g of product, mp 128 °C, (methyl ester 165 °C). More could be recovered from the solvents.

A solution of 9.2 g (0.1 mol) of propionyl chloride in 40 mL of benzene was added to 66.8 g (0.2 mol) of ethyl triphenylphosphoranylidene acetate in 500 mL of benzene with stirring. After 3 h the precipitate which had formed was removed by filtration. Some starting phosphorane can be recovered from this salt. The solution was concentrated by evaporating most of the benzene. Ether was added, and, when crystallization was complete, the ethyl 3-oxo-2-triphenylphosphoranylidene valerate was collected on a filter, mp 123 °C.[36] Pyrolysis of this material produced ethyl pent-2-ynoate as follows. The material was placed in a 100-mL flask fitted with a Vigreux column and a dry-ice-cooled trap. The contents of the flask were heated to 260–280 °C while maintaining the apparatus at 0.1–0.2 mm pressure. Distillate was collected for 3 h to yield 7.2 g (85%) of ethyl pent-2-ynoate. The ester, without further purification, was washed into a 100-mL flask with 3 mL of methanol. Then 50 mL of water and 6 g of KOH were added. The mixture (two phases) was stirred efficiently and heated for 1.5 h. The mixture, which was then homogeneous, was concentrated on a rotary evaporator, neutralized with excess HCl, and continuously extracted with ether. After evaporation of the ether, liquid pent-2-ynoic acid remained. It was treated with 40 mL of water and 7 g of KOH and heated to 90–100 °C (steam bath) for 3 h. After acidification with HCl and continuous ether extraction, pent-3-ynoic acid[37] was recovered. Hydrolysis of pent-2-ynoic ester and isomerization could not be accomplished in one step. Attempts to do so resulted in decarboxylation. The pent-3-ynoic acid, mp 102°, was fractionally crystallized from ether–pentane mixtures. Residues from the mother liquors were mixed with subsequent batches for isomerization by treatment with KOH.

Several batches of 1-pent-3-ynoic acid were mixed (20 g) and treated with diazomethane in ether. The ester was not isolated but was treated with lithium aluminum hydride (6 g) in ether. Hydrolysis of the complex was accomplished with dilute HCl. The ether layer was recovered. Ether was evaporated and the pent-3-ynol was distilled, bp 27 °C (1 mm).

For the synthesis of 1-pent-3-ynol-*1*-^{14}C, ethyl bromoacetate-*1*-^{14}C was used[38] as the starting material. When 1-pent-3-ynol-*3*-^{14}C was prepared, propionyl-*1*-^{14}C chloride was used. For 1-pent-3-ynol-*1*-$^{2}H_2$, methyl pent-3-ynoate was reduced with lithium aluminum deuteride.

Preparation of the Trifluoromethanesulfonate Ester of 1-Pent-3-ynol-*3*-^{14}C. The following general procedure[16] was used for all isotope position isomers of the carbinol.

Dry Na_2CO_3, 25.3 g (0.2383 mol) was weighed into a flask. Then 56.8 g (0.2016 mol) of freshly distilled triflic anhydride was added. The flask was fitted with an efficient condenser and an addition funnel and cooled to −5 to −10°. The entire reaction was carried out in an N_2 atmosphere. While maintaining the temperature below −5°, 15.4 g (0.18 mol) of 1-pent-3-ynol-*3*-^{14}C was added dropwise over 1 to 2 h, the reaction mixture was maintained at the low temperature for 2 h, and then allowed to warm up overnight. The next day the inorganic salts were removed on a filter and washed well with dry CH_2Cl_2. The solvent and excess reagent were removed on a rotary evaporator at room temperature and the product was distilled at 10–15 mm, 60–65 °C. The yield of crude product was 98%; distilled material 90+%, bp 65 °C (11 mm). The heating bath temperature was maintained at 80 °C. Higher temperatures result in reduced yields. The product is unstable and must be kept cold.

Solvolysis of 1-Pent-3-ynyl Triflate (1b). General Procedure. Up to temperatures of 50 °C the solvolyses were carried out in glass containers fitted with Teflon septa; at higher temperatures sealed glass ampoules were used. In both cases the reactions were stirred with magnetic bars. To precooled solutions of solvent and buffer (prepared in the ratios given in Tables I–III) was added, with cooling and stirring, 0.2 mmol of the appropriate homopropargyl compound; the vessel was flushed with nitrogen, sealed, and immersed in a thermostated bath adjusted to the desired temperature. After the required reaction times, the samples were removed from the thermostated bath and cooled; the solvolysis product mixtures were subjected without further workup to gas chromatographic analysis for quantitative determination of the yield of each product. In order to identify the several products, the solvolyses were run on a larger scale (up to 0.1 mol), the products were separated either by preparative gas chromatography, by column chromatography, or by distillation. The proton NMR and infrared spectra of the following compounds are identical with those of authentic samples: pent-1-en-3-yne (**13**),[2] 1-pent-3-ynyl 2,2,2-trifluoroethyl ether (**17**),[2] and 2-methylcyclobutanone bis(2,2,2-trifluoroethyl) acetal (**16**).[2] Data for **14**, **5b**, and **7b** are given in Table VII.

Table VI. Carbon-14 Assays for Solvolyses Products of Various Isotope Position Isomers of 1-Pent-3-ynyl Triflate (1b)

	^{14}C assay MCi/mol	% reaction and postion isomer
(1)	2.854 ± 0.0074	100% 3-^{14}C
(2)	2.882 ± 0.014	10% 3-^{14}C
(3)	2.443 ± 0.011	100% 3-^{14}C, 1-$^{2}H_2$
(4)	2.027 ± 0.040	10% 3-^{14}C, 1-$^{2}H_2$
(5)	0.3812 ± 0.0008	100% 1-^{14}C
(6)	0.3646 ± 0.0007[a]	10% 1-^{14}C
(7)	0.3626 ± 0.0015[a]	10% 1-^{14}C

[a] The average value of 0.3636 was used in calculating the isotope effects.

Table VII

Ethyl 1-pent-3-ynyl ether (14)[16]		
^1H NMR δ (ppm)	1.2	(t, 3 H, CH_2–CH_3, *J* = 7 Hz)
	1.78	(t, 3 H, C–C–CH_3, *J* = 2.5 Hz)
	2.2–2.65	(m, 2 H, C–C–CH_2–)
	3.50	(t, 2 H, O–CH_2–CH_2-, *J* = 7.5 Hz)
	3.52	(q, 2 H, –CH_2–CH_3, *J* = 7 Hz)
2-Methylcyclobutenyl 2,2,2-trifluoroethyl ether (5b)		
^1H NMR: δ (ppm)	1.65	(m, 3 H, –CH_3)
	1.94	(m, 2 H, CH_2 from Vierring)
	2.49	(m, 2 H, CH_2 next to C–O–)
	4.10	(q, 2 H, –CH_2–CF_3, *J* = 8.5 Hz)
IR: 1700 (m) C=C-O, 1275 (m), 1075 (s) =C–O–C, 1170 (s) CF_3		
MS: *m/e* 166 (41%, M^+), 165 (10), 164 (12), 138 (12, –C_2H_4), 125 (33, –C_3H_5), 83 (76, –CH_2CF_3), 67 (93, -OCH_2CF_3), 57 (100, -CH_2CF_3, -C_2H_2)		
2-Methylcyclobutanone (7b)[16]		
^1H NMR: δ (ppm)	1.18	(d, 3 H, CH_3, *J* = 7.5 Hz)
	1.3–2.7	(m, 2 H, $CHCH_2CH_2$–)
	2.8–3.6	(m, 3 H, –CH_2C=O and C–H)
IR: 3000 (m), 1780 (s) C=O, 1100 (m), 1040 (m)		
MS: *m/e* 84 (41%, M^+), 56 (100, –CO)		

Solvolysis of the Triflate for Isotope Effect Studies. Dry sodium carbonate, 9.8 g (0.093 mol), was mixed with dry trifluoroethanol (100 g), and the flask was put into a thermostated bath (30 °C) and stirred. The triflate, 10.1 g (0.0463 mol), was added and after 20 min, 200 mL of a 50:50 mixture of water–ethanol was added and the contents of the flask was heated to 55 °C for 0.5 h. After cooling, the reaction mixture was acidified and 47 mL of a 0.13 M reagent solution of 2,4-dinitrophenylhydrazine was added. A precipitate formed. After 2 h 200 mL more water was added. The next day the precipitate was collected on a filter and washed with water. The solution was concentrated on a rotary evaporator and more product was collected. The total yield was 1.07 g; for 10% reaction 1.22 g was expected. The orange product was taken up in ether and treated with Norit; ethanol was added to the ether solution. A second crystallization yielded a product, mp 122 °C, which was saved for ^{14}C analysis. For the deuterium isotope effect experiment, 1 g of 1-pent-3-ynol-*3*-^{14}C-*1*-$^{2}H_2$ was mixed with 11 g of ordinary acetylenic carbinol. [The results shown in Scheme II were obtained by proton NMR determination (integration of the spectra) for positions 3 and 4 of **7b**. Within experimental error the hydrogen contents of positions 3 and 4 were equal, and one-half the value of that for nondeuterated 2-methylcyclobutanone.] The material was distilled and treated as described above. Radioactivity of starting materials was determined by solvolyzing a 1-g sample of the starting material for 2.5 days at ambient temperature and recovering the 2-methylcyclobutanone for ^{14}C analysis as the 2,4-dinitrophenylhydrazone as described above. The results of all carbon-14 assays are given in Table VI. The isotope effects ($^{14}k/^{12}k$) were calculated by dividing the molar radioactivities at 100% reaction by those at 10% reaction. The deuterium isotope effect $^{H}k/^{D}k$ was similarly obtained by dividing the result in line 3, Table VI, by that in line 4. The insignificant contribution to rate difference by the carbon-14 in the 3 position of the substrate was neglected.

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