5870-61-1; $Br_2$, 7726-95-6; $Cl_2$, 7782-50-5; $CH_2Cl_2$, 75-09-2; *neo*-$C_5H_{12}$, 463-82-1; *n*-$C_4H_{10}$, 106-97-8; $MeCO_2$, 13799-69-4; $EtCO_2$, 24446-96-6; *i*-$PrCO_2$, 54388-94-2; *t*-$BuCO_2$, 28149-41-9; H, 12385-13-6; $CHCl_3$, 67-66-3; 1,2-dibromo-2,2-dichloroethane, 75-81-0; 1,1-dibromobutane, 62168-25-6; silver acetate, 563-63-3; silver propionate, 5489-14-5; silver isobutyrate, 24418-71-1; silver pivaloate, 7324-58-5; 1-bromobutane, 109-65-9.

**Supplementary Material Available:** A listing of the results from reactions of all acyl hypobromites summarized in Table IX at various alkane concentrations (37 pages). Ordering information is given on any current masthead page.

# Vinyl Cations. 40. π- and σ-Routes to Vinyl Cations. Solvolyses of 2-Methylcyclohexenyl, Cyclopentylideneethyl, Hex-5-yn-1-yl, and Related Triflates[1]

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**Abstract:** 2-Methylcyclohexenyl triflate (**1**), cyclopentylideneethyl triflate (**2**), and hept-6-yn-1-yl triflate (**3**) were solvolyzed at various temperatures in water–alcohol mixtures, in TFE–water mixtures, in TFA, in TFIP, in HFIP, and in 100% TFE in the presence of various buffers and the resulting products were determined. The three reactants were also solvolyzed in a standard mixture (1:100:100 = triflate:TFE:$Na_2CO_3$) at various temperatures, and the yields of products were compared. The solvolysis products were shown to be under kinetic control. Internal return occurs. From the foregoing data it is concluded that triflates **1** and **2** solvolyze through vinyl cation intermediates without σ-participation, whereas **3** solvolyzes through π-participation. The results of the solvolyses of **1** and **2** can be explained through classical cations that interchange through a transition state, **25**, but that never reach equilibrium. The cations exist as oriented ion pairs in which the counterion partially controls product formation. Triflate **3** solvolyzes in TFE–$Na_2CO_3$ with anchimeric assistance, but there is no evidence for the bridged ion **25**. Four additional acyclic triflates (**6–9**), in which the triple bonds are three, four, and five carbons removed from the leaving group, were also solvolyzed and the results are discussed in terms of their mechanistic implications.

Vinyl cations[3,4] can be generated by heterolysis of vinyl esters[4] that contain appropriate leaving groups attached directly to the double bond, by the addition of electrophilic reagents to allenic or acetylenic bonds,[4] or by triple bond participation, as in the solvolysis of homopropargyl[2,5–9] triflate.

Just as with carbocations whose electron-deficient carbons are $sp^2$ hybridized, vinyl cations also rearrange[4] and exhibit internal return.[4] There is good evidence that nonclassical vinyl cations can exist, since cyclobutenyl nonaflate (nonafluorobutanesulfonate) solvolyzes 3720 times faster,[10,11] at 100 °C, than cyclohexenyl nonaflate. Cyclopentenyl nonaflate, under similar conditions, does not cleave its carbon–oxygen bond but instead undergoes a second-order solvolysis with oxygen–sulfur cleavage.[12]

We report here our results on the solvolyses of the triflates **1**, **2**, and **3** (Scheme I), as well as those of **6**, **7**, **8**, and **9**. Triflates

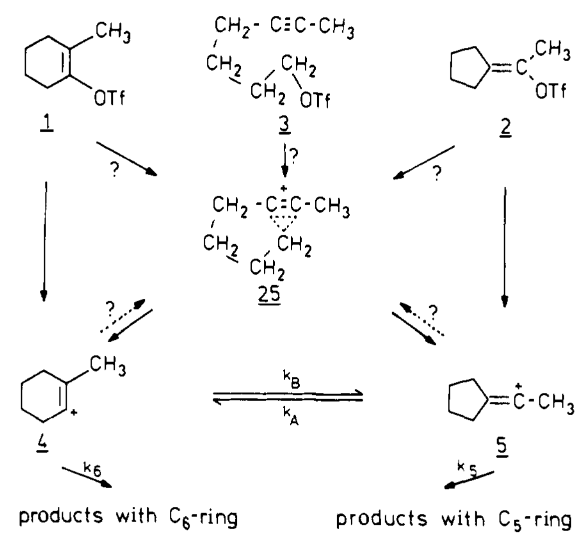
$HC{\equiv}CCH_2CH_2CH_2OTf$ **6**  $CH_3C{\equiv}CCH_2CH_2CH_2OTf$ **7**

$HC{\equiv}CCH_2CH_2CH_2CH_2OTf$ **8**

$HC{\equiv}CCH_2CH_2CH_2CH_2CH_2OTf$ **9**

**1**, **2**, and **3** should all be converted to many of the same products, although, as it turns out, not in the same proportions. The so-called "linear", secondary vinyl cation **5** is more stable[4] than the "bent" vinyl cation **4**, and consequently one might expect triflate **1**, in solvents of low nucleophilicity and high ionizing power, to exhibit considerable anchimeric assistance[13] through σ-participation. To the extent that triflate **2** rearranges to yield products containing six-carbon rings, anchimeric assistance is also conceivable. Further, triflate **3** cannot cyclize, during solvolysis, without π-participation of the triple bond, although the existence of such participation is not synonymous with nonclassical ions, or bridging, as has been pointed out by Winstein.[14]

Scheme I

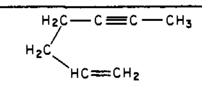
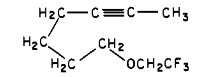
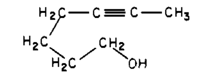
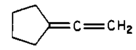
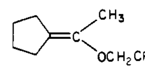
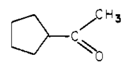
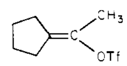
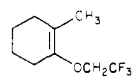
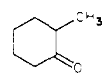
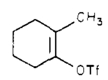



(1) Portions of this manuscript are from the Ph.D. Dissertation of K.-A. Fuchs, Universität des Saarlandes, Saarbrücken, 1978.
(2) Alexander von Humboldt, Senior-U.S. Scientist Award recipient, Feb. 1, 1982–Feb. 1, 1983.

(3) Hanack, M. *Angew. Chem.* **1978**, *90*, 346.
(4) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. "Vinyl Cations"; Academic Press: New York, 1979.
(5) Hanack, M.; Haffner, J.; Herterich, I. *Tetrahedron Lett.* **1965**, 875.
(6) Hanack, M.; Herterich, I.; Vött, V. *Tetrahedron Lett.* **1967**, 378.
(7) Hanack, M.; Bocher, S.; Herterich, I.; Hummel, K.; Vött, V. *Liebigs Ann. Chem.* **1970**, 733.
(8) Collins, C. J.; Benjamin, B. M.; Hanack, M.; Stutz, H. *J. Am. Chem. Soc.* **1977**, *99*, 1669.
(9) Hanack, M.; Collins, C. J.; Stutz, H.; Benjamin, B. M. *J. Am. Chem. Soc.* **1981**, *103*, 2356.
(10) Hanack, M.; Carnahan, E. J.; Krowczynski, A., Schobert, W.; Subramanian, L. R. *J. Am. Chem. Soc.* **1979**, *101*, 100.
(11) See also: Auchter, G.; Hanack, M. *Chem. Ber.*, in press.
(12) Hanack, M.; Bentz, H.; Märkl, R.; Subramanian, L. R. *Liebigs Ann. Chem.* **1978**, 1894.
(13) Winstein, S.; Lindgren, C. R.; Marshall, H.; Ingraham, L. L. *J. Am. Chem. Soc.* **1943**, *75*, 147.
(14) Winstein, S.; Grunwald, E. *J. Am. Chem. Soc.* **1948**, *70*, 835. Winstein, S.; Morse, B. K. *Ibid.* **1952**, *74*, 1134. Winstein, S.; Ingraham, *Ibid.* 1955, *77*, 1739. See also Collins et al.[15]
(15) Collins, C. J.; Bonner, W. A.; Lester, C. T. *J. Am. Chem. Soc.* **1959**, *81*, 466. Bonner, W. A.; Collins, C. J. *Ibid.* **1956**, *78*, 5587.

0002-7863/83/1505-4008$01.50/0 

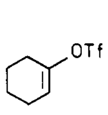
Table I. Solvolyses of 2-Methylcyclohexenyl Triflate (1): Variation of Product Ratio (Relative %) with Temperature[a]

| products | | temp, °C | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 80 | 90 | 100 | 110 | 120 | 150 | 180 |
|  | (**16**) | | | | | | <1 | <1 |
|  | (17) | | | | <0.1 | <0.1 | | |
|  | (18) | | | | <0.1 | <0.1 | <0.1 | |
|  | (19) | 2 | 2 | 4 | 4 | 4 | 3 | 4 |
|  | (20) | 38 | 38 | 39 | 39 | 39 | 26 | 28 |
|  | (21) | <1 | <1 | <1 | 1 | <1 | 10 | 8 |
|  | (2) | | | | | | | |
|  | (22) | 59 | 58 | 57 | 55 | 55 | 41 | 42 |
|  | (23) | <1 | <1 | <1 | 1 | <1 | 4 | 4 |
|  | (1)[b] | [87] | [79] | [19] | | | | |
| unidentified[c] | | | | | | | 15/25 | 13/21 |
| $m_5/m_6$[d] | | 0.68 | 0.69 | 0.74 | 0.79 | 0.77 | 0.86 | 0.87 |

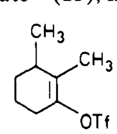
[a] Solvent, 100% TFE (1:TFE:$Na_2CO_3$ = 1:100:100). [b] Solvolysis stopped at % remaining triflate. [c] The numbers here represent the %/no. of peaks. [d] Ratio of 5-ring to 6-ring products.

By a comparison of the kinetics and product analyses in the solvolyses of these closely related starting materials (**1**, **2**, and **3**), we hoped to be able to draw some conclusions concerning the effect of possible σ- or π-participation on the progress of each reaction to determine whether or not all three reactions proceed through common intermediates and whether the intermediates can best be described as classical or nonclassical carbocations. By a comparison of the product analyses and (where necessary) the kinetics of the solvolyses of **6**, **7**, **8**, and **9**, we planned to study the effect of chain length on π-participation and cyclization tendency of triple bonds three, four, and five carbons distant from the leaving group.

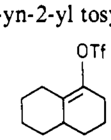
Previous experiments with cyclohexenyl triflate[16-18] (**10**), tosylate,[19,20] and brosylate[19,20] and with **1**,[19] **11**,[16] and **12**[17,21] have been performed; the ethanolysis of **2** was examined,[22] and 6-phenylhex-5-yn-1-yl brosylate[23] (**13**), hept-6-yn-2-yl tosylate[24,25] (**14**), and oct-6-yn-2-yl tosylate[25] (**15**) have all been solvolyzed in acetic or formic acids (or both). Our own results, together with some of the results of previous investigations,[16-25] will be discussed later in this paper.



10



11



12

(16) Hummel, K. Ph.D. Dissertation, Tübingen, 1971.
(17) Pfeiffer, W. D.; Bahn, C. A.; Schleyer, P. v. R.; Bocher, S.; Harding, C. E.; Hummel, K.; Hanack, M.; Stang, P. J. *J. Am. Chem. Soc.* **1971**, *93*, 1513.
(18) Dueber, T. E.; Stang, P. J.; Pfeiffer, W. D.; Summerville, R. H.; Imhoff, M. A.; Schleyer, P. v. R.; Hummel, K.; Bocher, S.; Harding, C. E.; Hanack, M. *Angew Chem.* **1970**, *82*, 517.
(19) Peterson, P. E.; Indelicato, J. M. *J. Am. Chem. Soc.* **1968** *90*, 6515.
(20) Peterson, P. E.; Casey, C., Tao, E. V. P.; Agtarap, A.; Thompson, G. *J. Am. Chem. Soc.* **1965**, *87*, 5163.
(21) Chandy, M. J.; Subramanian, L. R.; Hanack, M. *Chem. Ber.* **1975**, *108*, 2212.
(22) Schleyer, P. v. R., personal communication.
(23) Closson, W. D.; Roman, S. A. *Tetrahedron Lett.* **1966**, 6015.

## Results

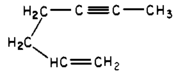
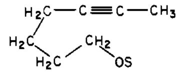
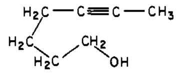
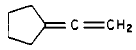
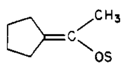
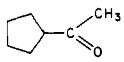
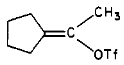
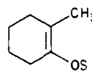
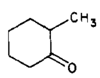
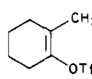
The syntheses of all starting materials are given in the Experimental Section. Conditions for the solvolyses of the three triflates **1**, **2**, and **3** by $S_N1$ mechanisms, with kinetic control, under which all solvolysis products were stable, had to be carefully worked out.[26] Several solvents and buffers were tested; one system was found that met all the requirements and that in addition, allowed the solvolysis products to be directly analyzed by GC without workup; this system consists of one part triflate (**1**, **2**, or **3**), 100 parts each trifluoroethanol and sodium carbonate, and one part tetralin (NMR standard). Two glass capillary columns of different polarities (SE 30, K 20 M) were employed. The columns were equipped with a flame ionization detector (FID), and the intensities were automatically integrated and printed. Because of the structural similarities of the products, all intensities are uncorrected with respect to their response factors.

The solvolysis products were, with a few exceptions, purified by preparative GC and identified by means of proton NMR, infrared, and mass spectrometry. When a given product could not be purified because of low concentration or incomplete GC separation, it was identified through GC/MS or mixed injection with an authentic sample on two different capillary columns of different polarities.

**Kinetic Measurements of Solvolysis Rates of 1, 2, and 3.** In order to find a temperature range in which the three triflates (**1**,

(24) Peterson, P. E.; Kamat, R. J.; *J. Am. Chem. Soc.* **1966**, *88*, 3152.
(25) Peterson, P. E.; Kamat, R. J. *J. Am. Chem. Soc.* **1969**, *91*, 4521.
(26) For details see: Fuchs, K.-A. Ph.D. Dissertation, Tübingen, 1978, pp 14–21.

Table II. Solvolyses of 2-Methylcyclohexenyl Triflate (1): Variation of Product Ratio (Relative Percent) with Solvent[a]

| products | | solvent (temp, °C) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 100% EtOH (130)[b] | 60% EtOH (125)[c] | $H_2O$ (130)[d] | 80% TFE 100[e] | 97% TFE 100[e] | 100% TFE 100[e] | abs. HFIP 100[e] | 100% TFA 100[f] |
|  | (16) | 21 | <0.1 | 4 | <0.1 | <0.1 | | 2 | |
|  | (17) | | <0.1 | | <0.1 | <0.1 | <0.1 | | |
|  | (18) | | <0.1 | <1 | <0.1 | <0.1 | | | |
|  | (19) | 4 | <1 | 3 | 2 | 4 | 3 | 2 | |
|  | (20) | 5 | | | 12 | 31 | 39 | 32 | 2 |
|  | (21) | <0.1 | 27 | 27 | 15 | 5 | <1 | <1 | 14 |
|  | (2) | | | | | | | | |
|  | (22) | 39 | | | 29 | 50 | 56 | 59 | 17 |
|  | (23) | 25 | 63 | 62 | 39 | 7 | 1 | 2 | 61 |
|  | (1) | | | | | | | | |
| unidentified[g] | | | 9/4 | | 4/9 | 3/5 | 3/4 | 2/6 | 6/1 |
| $m_5/m_6$[h] | | 0.14 | 0.40 | 0.48 | 0.40 | 0.70 | 0.74 | 0.57 | 0.20 |

[a] The base is $Na_2CO_3$ unless otherwise stated. [b] 3 days. [c] 2 days, base = 2,6-lutidine. [d] 2.5 days. [f] 1 day, buffer = $NaOOCCF_3$, hydrolyzed with NaOH before the analysis. [g] The numbers given represents %/no. of peaks. [h] Ratio of 5-ring to 6-ring products.

2, and 3) could be solvolyzed in 100% TFE under as nearly identical conditions as possible and in order to estimate how long to allow each reaction to proceed to completion (at least 20 half-lives), we carried out certain kinetic measurements[27,30] on the triflates **2** and **3**. Results were evaluated by the Guggenheim method,[28] but in the interest of brevity are not recorded here since they are available elsewhere.[1] The kinetics of **1** in various solvents have been reported previously.[17]

**Solvolysis of 2-Methylcyclohexenyl Triflate (1).** The products from the solvolyses of 2-methylcyclohexenyl triflate (**1**) in 100% TFE with $Na_2CO_3$ buffer (**1**:TFE:$Na_2CO_3$ = 1:100:100) were determined at temperatures from 80 to 180 °C. The results are given in Table I and demonstrate a negligible temperature effect up to 120 °C and a very small effect between 120 and 180 °C. A second series of experiments (Table II) illustrates how the product distribution varies with changing solvent nucleophilicity, and a third series (Table III) portrays the variations experienced with changing concentrations of added buffers in both TFE and HFIP solvents.

From the constancy of the product ratios up to 120 °C (Table I) we conclude that the solvolyses in TFE are under kinetic control, a fact that had to be established before any mechanistic conclusions can be drawn from the product analyses. From Table II it can be seen (from the ratio $m_5/m_6$) ($m_5$ = moles of compounds with five carbons in ring, etc.) that as the solvent nucleophilicity decreases the percent rearrangement to 5-ring products increases, with the notable exception of the solvents HFIP and TFA.

HFIP, which is a considerably stronger acid than TFE, reacts with $Na_2CO_3$ to give the hexafluoro-2-propanoate anion, which increases the nucleophilicity of the solvent and thus decreases the rearrangement (see Discussion). The situation with regard to TFA is not so easily explained.

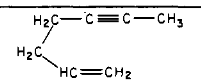
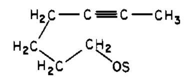
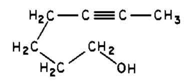
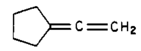
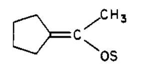
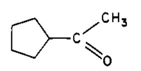
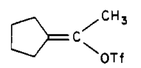
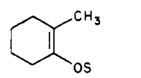
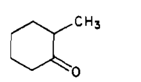
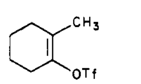
We were not able to repeat the observation[17] that in 60% ethanol there is more 5-ring product than 6-ring product formed ($m_5/m_6$ = 1.5, 125 °C). From Table II it is clear that our value ($m_5/m_6$ = 0.40, 125 °C) fits in well with the values (0.14 and 0.48) observed for ethanol and water, respectively.

All attempts to increase the fraction of rearrangement by adding $NaOSO_2CF_3$ failed.

**Solvolyses of Cyclopentylideneethyl Triflate (2).** Triflate **2** was also solvolyzed (in TFE with $Na_2CO_3$) at various temperatures. The results are portrayed in Table IV. Since 2-methylcyclohexenyl triflate (**1**) was recovered in all four experiments through the internal return process in yields of 2–3%, the question arises whether some of the products of solvolysis of **2** could have been produced through solvolysis of **1**. This possibility was ruled out by a determination of the specific reaction rate constants under the same conditions of solvent and buffer for **1** ($k = 7.2 \times 10^{-6}$ $s^{-1}$) and **2** ($k = 9.5 \times 10^{-3}$ $s^{-1}$)[29] at 120 °C. Since **2** solvolyzes nearly 1400 times faster than **1**, the solvolysis products expected from **1** amount to less than 1%. Triflate **2** was also solvolyzed in a variety of solvent mixtures and the products were determined.

(27) Schneider, H.-J.; Schneider-Bernlöhr, H.; Hanack, M. *Liebigs Ann. Chem.* **1969**, *722*, 234.
(28) Guggenheim, A. E. *Philos. Mag.* **1926**, *1*, 538.
(29) Calculated from the data of: Summerville, R. H., Senkler, C. A.; Schleyer, P. R.; Dueber, T. E.; Stang, P. E., *J. Am. Chem. Soc.* **1974**, *96*, 1100.
(30) Roberts, R. M. G. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1183.
(31) Coke, J. L.; McFarlane, F. C.; Mourning, M. C.; Jones, M. G. *J. Am. Chem. Soc.* **1969**, *91*, 1154.
(32) Cram, D. J. *J. Am. Chem. Soc.* **1949**, *71*, 3863, 3875.
(33) In the solvolyses of ethyl and 2-phenylethyl tosylates, it was found that $k_t(PhCH_2CH_2OTS)/k_t(EtOTS)$ increased from 0.24 to 1770 between ethanol and TFA, respectively (Schadt, F. L.; Lancelot, C. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1978**, *100*, 228).

Table III. Solvolyses of 2-Methylcyclohexenyl Triflate (**1**): Variation of Product Ratio (Relative Percent) with Added Salts as Buffers in TFE and Hexafluoroisopropyl Alcohol (HFIP)

| products | | solvent (temp, °C; base; pH) | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | | 100% TFE (130; $CaCO_3$; ~7) | 100% TFE (130; $Na_2CO_3$; ~5) | 100% TFE (130; *a*) | 100% TFE (100; $Na_2CO_3$) | 100% TFE (100; *b*) | abs HFIP (100; $Na_2CO_3$) | abs HFIP (100; *b*) |
|  | (**16**) | | | | | <0.1 | 2 | 6 |
|  | (**17**) | | <0.1 | | <0.1 | | | |
|  | (**18**) | | | | | | | |
|  | (**19**) | | 4 | 8 | 4 | 7 | 2 | 10 |
|  | (**20**) | | 33 | 34 | 39 | 37 | 32 | 30 |
|  | (**21**) | 35 | 5 | 5 | <1 | 2 | 1 | 3 |
|  | (**2**) | | | | | | | |
|  | (**22**) | | 53 | 34 | 57 | 44 | 59 | 31 |
|  | (**23**) | 58 | 2 | 7 | 1 | 9 | 2 | 4 |
|  | (**1**) | | | | [51] | [58] | [54] | [26] |
| unidentified[c] | | 7/6 | | 11/7 | | 1/4 | 2/6 | 13/4 |
| $m_5/m_6$[d] | | 0.6 | 0.77 | 1.1 | 0.74 | 0.87 | 0.57 | 1.26 |

[a] Base concentration = 100 equiv in all cases, Base = 1 M $NaOCH_2CF_3$. [b] Base = $Na_2CO_3$ + $K_2CO_3$ (50:50). [c] The numbers given here represent %/no. of peaks. [d] Ratio of 5-ring to 6-ring products.

The results are given in Table V. The most notable conclusion from Table V is that as the nucleophilicity of the solvent decreases the fraction of 6-ring product increases [$m_5/m_6$ decreases].

**Solvolyses of Hept-5-yn-1-yl Triflate (3).** As in the case of triflates **1** and **2**, triflate **3** was also solvolyzed at various temperatures (−10 to 30 °C) and in various solvents and solvent mixtures. Results are shown in Tables VI and VII, respectively. The most striking result from Table VI is the variation of internal return (to the triflates **1** and **2**) with temperature. At −10 °C, the ratio **2**:**1** is 44, whereas at 10–30 °C, it settles down to about 13–14, although the ratio of the remaining 5-ring and 6-ring products (**20** + **21**):(**22** + **23**) remains fairly constant at 3–4. From Table VII the enormous variation of $k_\Delta/k_s$ ($k_\Delta$ = specific reaction rate constant for participation of triple bond, $k_s$ = constant for $S_N2$ reaction[31]) with nucleophilicity of solvent can be seen.

Finally, the triflates **6**, **7**, **8**, and **9** were solvolyzed in TFE ($Na_2CO_3$ buffer) at 0 or 60 °C for periods of time sufficient to ensure 20 half-lives for each reaction. The results are given in Table VIII; in addition the kinetics of the solvolyses of the hex-5-yn-1-yl (**8**), cyclohexenyl (**10**), and hept-6-yn-1-yl (**9**) triflates were measured. The results are given in Table IX together with the literature[17] values for cycloheptenyl triflate (**24**).

## Discussion

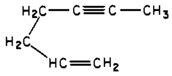
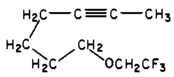
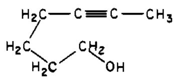
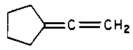
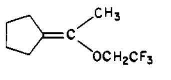
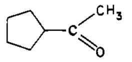
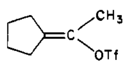
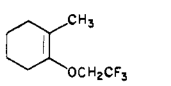
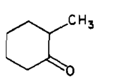
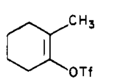
From Tables II and V, which portray the effect of change in solvent upon product ratio in the solvolyses of **1** and **2**, it is clear that in solvents of low nucleophilicity there is more rearrangement than in solvents of high nucleophilicity. Further, the tendency to rearrange increases with temperature (Tables I and IV), although at all temperatures investigated the intermediates from one or both of the triflates **1** and **2** failed to reach equilibrium before going respectively to 5-ring or 6-ring products. As a first approximation to rationalizing the mechanism we may consider Scheme I, in which the vinyl cations **4** and **5** are shown as intermediates between **1** and **2** and their respective cyclic products. At this point neither ion pairs nor the various types of ion-pair return are considered. The ratios $m_5/m_6$ for the products of trifluoroacetolysis of **1** and **2** at 110 °C are 0.79 and 16.4, respectively (Tables I and IV; $m_5/m_6$ = ratio of products containing a $C_5$ ring to those containing a $C_6$ ring). From Table VI we can easily extrapolate the values $m_5/m_6$ from **3** to 110 °C, at which temperature $m_5/m_6$ = 5. It thus appears that classical cation **4**, formed from **1**, reacts with nucleophile to yield 6-ring products faster than it rearranges to classical cation **5**. Likewise **5**, formed on solvolysis of **2**, goes directly to 5-ring products faster than it rearranges to **4**. We conclude, therefore, that triflates **1** and **2** do not proceed to a common intermediate, for if they did the ratios $m_5/m_6$ from **1** and **2** should be identical. The mechanism shown, therefore, in Scheme I is completely compatible with the results, provided we ignore **25** and the arrows leading from and to it and the cations **4** and **5**. It is tempting to assume that the value $m_5/m_6$ = 5 represents the situation at 110 °C when cations **4** and **5** are at equilibrium.

From Scheme I the following two equations can easily be derived, eq 1 representing the situation for triflate **1**, and eq 2 that for triflate **2**. From the values (vide supra) $m_5/m_6$ = 0.79

$$\frac{m_5}{m_6} = \frac{k_B/k_6}{(k_A/k_5) + 1} \quad (1)$$

$$m_5/m_6 = k_5/k_A[(k_B/k_6) + 1] \quad (2)$$

Table IV. Solvolyses of Cyclopentylideneethyl Triflate (**2**): Variation of Product Ratio (Relative Percent) with Temperature[a]

| products | | temp, °C; time | | | |
|---|---|---|---|---|---|
| | | 25; 4 days | 60; 1 day | 70; 1 day | 110; 30 min |
|  | (16) | | | | <0.1 |
|  | (17) | <0.1 | <0.1 | <0.1 | <0.1 |
|  | (18) | <0.1 | | <0.1 | <0.1 |
|  | (19)[b] | <1 | 1 | 4 | 4 |
|  | (20) | 96 | 89 | 85 | 3 |
|  | (21) | <1 | 2 | 2 | 79 |
|  | (2)[c] | [50] | | | |
|  | (22) | <1 | 2 | 2 | 1 |
|  | (23) | | | 1 | 2 |
|  | (1) | 2 | 3 | 3 | 2 |
| unidentified[d] | | 2/2 | 5/3 | 3/4 | 8/6 |
| $m_5/m_6$ | | 39.0 | 18.2 | 16.3 | 16.4 |
| internal return, % | | 2 | 3 | 3 | 2 |
| rearrangement to 6-ring, % | | 3 | 5 | 6 | 4 |

[a] Solvent, 100% TFE (1:TFE:$Na_2CO_3$ = 1:100:100). [b] Not considered in calculating $m_5/m_6$, since elimination from the triflate is possible. [c] Reaction stopeed at % remaining triflate. [d] The numbers given here represent %/no. of peaks.

(from **1**) and $m_5/m_6$ = 16.4 (from **2**), we can now calculate that $k_A/k_5$ = 0.114 and $k_B/k_6$ = 0.88, which are measures of the relative rates by which cations **4** and **5** react with solvent or rearrange to their isomeric vinyl cations.

From the kinetics of the trifluoroethanolyses of **1**, **2**, and **3** as well as from their product analyses, it can be seen that the reaction of **3** is different from those of **1** and **2**: Neither **1** nor **2** shows any tendency for anchimeric assistance through σ-participation in that the product analyses (vide supra) are compatible with classical cation intermediates formed without bridging. Triflate **3** at 30 °C, however, solvolyzes[1] 1000 times faster (97% TFE) than does **1** at 125 °C (80% TFE) and 160 times faster than does **2** at 60 °C (97% TFE).

A workable hypothesis for the trifluoroethanolysis of triflates **1** and **2** is that they go respectively to the classical vinyl cations **4** and **5**, which partially equilibrate through transition state **25**; **25**, formed directly from **3**, goes directly to the classical cations **4** and **5**, which are converted to products. Structure **25** is a transition state between the classical cations **4** and **5** and is also the transition state resulting from the $k_\Delta$ component in the solvolysis of **3**. This is equivalent to postulating that the transition state **25** is the branching point, during the solvolysis of **3**, for production of the two cations **4** and **5**. A possible way out of this dilemma is to propose that **25** (from **3**) goes directly (for example) to **5** which rearranges to **6** with a different value of $k_B/k_A$ than when these two cations are generated either from **1** or **2**. These differences in $k_B/k_A$ could be due to counterion effects,[34] since upon solvolysis of **3** the triflate anion should be oriented quite differently with respect to the two cations **4** and **5**, than during the solvolyses of **1** or **2**.

It is clear that both thermodynamic and kinetically controlled processes take place. Reactants **1** and **2** can return to both **1** and **2**. Triflate **3** also produces **1** and **2** through the thermodynamic process but does not return to itself. All other products are kinetically controlled. At higher temperatures (100 °C), **1** yields no **2** (Table I) because **2** solvolyzes at 100 °C about 1400 times faster than **1**. At 25 °C, **2** yields 2% **1** (Table IV). At 0 °C, **3** yields 80% **2** and 3% **1** (Table VI). The most striking result in this respect is recorded in Table VI for the solvolysis (TFE) of **3** as a function of temperature (−10 to 30 °C). Here the percentage of returned **1** remains reasonably constant, whereas the percentage of returned **2** is significantly higher at the lower temperature.[35] The ratios of the other 5- to 6-ring products (i.e., those under kinetic control) are also relatively constant.

Triflates **6** and **7** (Table VIII) undergo no cyclization, but they solvolyze even in 100% TFE through $S_N2$ mechanisms. The ring strain in the cyclopentenyl cation must be so high that it cannot form under these conditions. It is well-known,[8-10] however, that homopropargyl triflates readily cyclize, lending support to the assumption of a nonclassical structure for the cyclobutenyl cation. Triflate **8**, in 100% TFE, exhibits a reduced tendency to rearrange ($k_\Delta/k_s$ = 0.6), when compared with **3**, whereas **9** rearranges even more weakly ($k_\Delta/k_s$ = 0.2). Comparisons of the specific reaction rate constants (30.0 °C, 97% TFE) of **3**[1] and **8**[1] (Table IX, $k_3/k_8$ = 60) and the $k_\Delta/k_s$ ratios (0.6 vs. 100, respectively) illustrate the remarkable enhancing effect on $k_\Delta$ of the terminal methyl in triflate **3**.[3]

In summary, the two triflates **1** and **2** undergo trifluoroethanolysis (and some other solvolyses as well) through vinyl cations (**4** and **5**) that go to products faster than they equilibrate with each other. There is no evidence for σ-participation. Triflate **3** solvolyzes much faster and at lower temperature than either **1** or **2** and shows evidence of anchimeric assistance through π-participation ($k_\Delta$). The reluctance for rearrangement of both **4** and **5** is consistent with (1) a certain configuration-holding capacity of the counterions at the solvent-separated ion-pair stage, (2) a lack of σ-participation, and (3) a bridged structure (**25**)[36] that must be a transition state rather than a bridged ion; at least, it cannot be lower in energy than the classical ions **4** and **5**. Ion-pair return was demonstrated in the reactions of **1** and **2**, and this must occur at the intimate ion-pair stage. The solvolysis products are formed through kinetically controlled processes, whereas internal return to triflates **1** and **2** occurs through processes that are thermodynamically controlled.

Triflates **6** and **7** do not cyclize in 100% TFE (no $k_\Delta$) but instead undergo $S_N2$ processes ($k_s$), illustrating that cyclopentenyl type vinyl cations are too strained to be formed under the conditions employed. As one proceeds from triflates **3** to **8** to **9**, $k_\Delta/k_s$ (100% TFE, 0 °C) decreases from over 300 (**3**) to 0.6 (**8**) to 0.2 (**9**), which indicates the enhancing effect on $k_\Delta$ of the terminal methyl in **3** as well as the fact that, with the exception of homopropargyl triflate, the triple bond in **8** seems to be most favorably situated to provide anchimeric assistance.

(34) Collins, C. J. *Chem. Soc. Rev.* **1975**, *4*, 251. Kirmse, W.; Siegfried, R. *J. Am. Chem. Soc.* **1983**, *105*, 950. Bly, R. S.; Bly, R. K.; Hamilton, J. B.; Jindal, S. P. *Ibid.* **1977**, *99*, 204. Bly, R. S.; Bly, R. K.; Hamilton, J. B.; Hsin, J. C. N.; Lillis, P. K. *Ibid.* **1977**, *99*, 216. Collins, C. J. *Ibid.* **1979**, *101*, 1878.

(35) See also: Patch, R.; Margosian, D. *J. Am. Chem. Soc.* **1976**, *98*, 6746. Stang, P. J.; Dueber, T. E. *Tetrahedron Lett.* **1977**, 563.

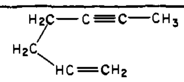
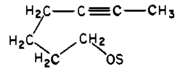
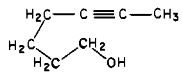
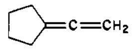
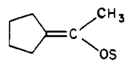
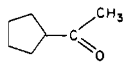
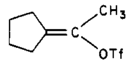
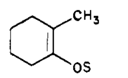
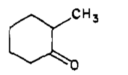
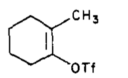
(36) Isotope effects can aid in such problems: Ando, T.; Kim, S. G.; Matsuda, K.; Yamataka, H.; Yukawa, Y.; Fry, A.; Lewis, D. E.; Sims, L. B.; Wilson, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 3505.

(37) Frydman, N.; Bixon, R.; Sprecher, M.; Mazur, Y. *Chem. Commun.* **1969**, 1044.

(38) Zelinsky, N.; Generesow, A. *Ber. Dtsch. Chem. Ges.* **1896**, *29*, 729.

(39) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, H. D. *J. Org. Chem.* **1969**, *34*, 2324.

Table V. Solvolysis of Cyclopentylideneethyl Triflate (**2**): Variation of Product Ratio (Relative Percent) with Solvent

| | solvent, reaction conditions | | | | | | |
|---|---|---|---|---|---|---|---|
| products | 80% EtOH, *a* | 50% EtOH, *b* | 80% TFE, *a* | 97% TFE, *a* | 100% TFE, *a* | abs HFIP, *a* | 100% TFA, *c* |
|  (**16**) | | | | | | | |
|  (**17**) | | | <0.1 | <0.1 | <0.1 | <0.1 | |
|  (**18**) | | | <0.1 | <0.1 | | | |
|  (**19**) | 24 | | 3 | 6 | 4 | 11 | |
|  (**20**) | 28 | | 42 | 79 | 89 | 49 | |
|  (**21**) | 29 | >99 | 52 | 10 | 2 | 3 | 93 |
|  (**2**)$^d$ | [16] | | | | | | |
|  (**22**) | <1 | | 1 | 1 | 2 | 11 | |
|  (**23**) | | | <0.1 | <0.1 | | <0.1 | 2 |
|  (**1**) | 2 | | 2 | 3 | 3 | 4 | 5 |
| unidentified$^e$ | | | | 1/1 | | 20/5 | |
| $m_5/m_6$ | 60.0 | | 37.6 | 23.0 | 18.2 | 3.7 | 13.4 |
| internal return, % | 2 | | 2 | 3 | 3 | 4 | 5 |
| rearrangement to 6-ring, % | 2 | | 3 | 4 | 5 | 14 | 7 |

$^a$ 60 °C, 1 day. $^b$ 75 °C, 2 h. $^c$ 30 °C, 1 day, buffer: $NaOOCCF_3$, hydrolyzed before analysis with NaOH. $^d$ Solvolysis stopped with % remaining triflate. $^e$ The %/no. of peaks are given.

## Experimental Section

**Experimental Methods.** (1) Gas chromatography was carried out with the following equipment: (a) Hewlett-Packard HP 5750 (FID and WLD); (b) HP 5721 (FID); (c) HP 5722 (WLD); (d) Carlo Erba 2301 Ac with LT programmer 220 as FID; (e) Varian P 90 (WLD). The usual packed glass columns were available as well as glass capillary columns (25 m) covered with Carbowax and SE 30. Results were evaluated with an HP 3385A integrator. (2) Mass spectroscopy was done with Varian MAT 311 and MAT 711 with and without GC/MS coupling and with GC/MS LKB and MS 9 from AEI Manchester. (3) For NMR spectroscopy, Varian A-60, EM 360, Brucker WP-60, HX-90, and HFX-90 were available for $^1$H NMR. For $^{13}$C NMR we used Brucker WP-60, HX-90, and HFX-90 instruments. (4) Infrared spectra were taken on Beckman IR 4 and Phillips PYE-Unicam SP 1000 spectrometers. (5) Kinetic measurements during solvolyses were performed with Combititrators 3D (E 512, E 425, and E 473) (Methrohm). A Colora thermostated bath type NB/05 was employed for temperature control (±01 °C).

**2-Methylcyclohexenyl Triflate (1).** The general procedure[16,18,37] for preparing triflates from ketones led to an 85% yield of a mixture of 78% 2-methylcyclohexenyl triflate (**1**) and 22% of the isomer 6-methylcyclohexenyl triflate. The isomers could be separated, but only with difficulty and with low yields. Consequently 2-methylcyclohexanone[38] was dissolved in 25 mL of dry DMF and then treated with a mixture of 8.1 g (0.75 mol) of chlorotrimethylsilane and 10.1 g (0.1 mol) of TEA.[39] After 48 h at 60 °C the reaction mixture was cooled, diluted with 100 mL of petroleum ether (30–50), and poured into ice water. The organic phase was washed twice with water and then twice each with aqueous $NH_4Cl$ and with aqueous $NaHCO_3$. The resulting solution was dried over $MgSO_4$ and concentrated; yield 85%. The two isomers were in the ratio 78:22. The 2-methylcyclohexenyl trimethylsilyl ether was easily separated by distillation through a spinning-band column. $^1$H NMR δ 0.14 (s, 9 H, $Si(CH_3)_3$), 1.5 (s, 3 H, $CH_3$), 1.4–1.7 (m, 4 H, $CH_2$, C-4, C-5), 1.8–2.2 (m, 4 H, $CH_2$, C-3, C-6).

The triflate **1** was prepared from the trimethylsilyl ether by the procedure of Bergman:[40] yield 65%; $^1$H NMR δ 1.8 (s (br), 7 H, $CH_3$ and $CH_2$, C-4, C-5), 2.1–2.5 (m, 4 H, $CH_2$, C-3, C-6); $^{13}$C NMR δ 16.66 (C-7), 21.94 (C-4), 23.40 (C-5), 27.77 (C-3), 30.80 (C-6), 118.66 (q, $J_{CF}$ = 319.4 Hz, $CF_3$), 126.01 (C-2), 143.61 (C-1); IR (cm$^{-1}$) 945 (sym $C—OSO_2$), 1045 (S—O), 1150 (sym S=O), 1225 (C—F), 1255 (asym $C—OSO_2$), 1420 (asym S=O), 1720 (C=C).

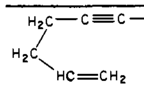
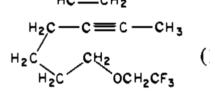
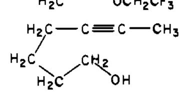
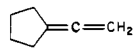
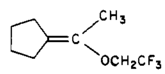
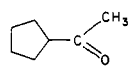
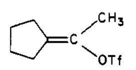
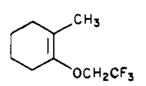
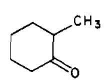
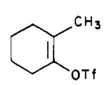
**Solvolyses of 2-Methylcyclohexenyl Triflate (1).** In a typical experiment (for example, solvolysis in 100% TFE), 5 μL (0.025 mmol) of **1** was dissolved in 200 μL (2.5 mmol) of 100% TFE containing 250 mg (2.5 mmol) of $Na_2CO_3$ and tetralin (0.025 mmol) as a standard. The solutions were under nitrogen. The reaction vessel was a 8 × 1.5 mm glass ampule. The TFE had been distilled over $P_2O_5$ and finally over $Na_2CO_3$. When preparative separation of components was necessary, proportionately larger quantities could be used. Temperature control was maintained with a Colora bath type NB/05 (±01 °C).

After 20 half-lives the $Na_2CO_3$ was removed by centrifugation, and the remaining solution was subjected directly to GC analysis. The solvolysis products were identified by one or more of the following methods: $^1$H NMR, IR, GC/MS, comparison with an authentic sample, or hydrolysis (in case of an ether or ester) to known products. A preparative separation of cyclopentylideneethyl trifluoroethyl ether (**20**) was unsuccessful, so it was hydrolyzed to the ketone (**23**). Before hydrolysis, however, the sample containing **20** was subjected to GC/MS: MS, *m/e* 194 (59%, M$^+$), 179 (100, M$^+$ − $CH_3$), 166 (30, M$^+$ − $C_2H_4$), 165 (38 M$^+$, − $C_2H_5$), 111 (9, M$^+$ − $CH_2CF_3$), 95 (15, M$^+$ − $OCH_2CF_3$).

Analytical data for 2-methylcyclohexanone (**23**): $^1$H NMR δ 0.95 (d, 3 H, $CH_3$, $^3J$ = 6 Hz), 1.4–2.0 (m, 6 H, $CH_2$, C-3, C-4, C-5), 2.0–2.5 (m, 3 H, methine H, $CH_2$, C-6); IR (cm$^{-1}$) 1735 (C=O); MS, *m/e* 112 (66%, M$^+$), 97 (14, M$^+$ − $CH_3$), 94 (6, M$^+$ − $H_{20}$), 84 (32, M$^+$ − CO),

(40) Clark, T. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1974,** *96,* 7934. see also: Chandy, M. J.; Subramanian, L. R.; Hanack, M. *Chem. Ber.* **1975**, *108*, 2212.

Table VI. Solvolyses of Hept-5-yn-1-yl Triflate (3): Variation of Product Ratio (Relative Percent) with Temperature

| products | | temp, °C | | | | |
|---|---|---|---|---|---|---|
| | | −10 | 0 | 10 | 20 | 30 |
|  | (16) | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
|  | (17) | <0.1 | <0.1 | <0.1 | <0.1 | <1 |
|  | (18) | <0.1 | <0.1 | <0.1 | <0.1 | <1 |
|  | (19) | 1 | 1 | 1 | 2 | 3 |
|  | (20) | 7 | 10 | 23 | 22 | 24 |
|  | (21) | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
|  | (2) | 88 | 79 | 63 | 62 | 58 |
|  | (22) | 2 | 4 | 8 | 9 | 10 |
|  | (23) | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
|  | (1) | 2 | 3 | 5 | 5 | 4 |
| unidentified[a] | | 1/1 | | | | |
| $m_5/m_6$ | | 24.0 | 13.0 | 6.6 | 6.1 | 5.8 |
| internal return[b] | | 44.0 | 26.0 | 12.6 | 12.4 | 14.5 |
| $m_{20+21}/m_{22+23}$ | | 4.0 | 3.0 | 2.9 | 3.0 | 2.4 |
| total % 5-ring | | 96 | 90 | 87 | 86 | 86 |
| total % 6-ring | | 4 | 7 | 13 | 14 | 14 |

[a] The values represent %/no. of peaks. [b] Ratio of moles of triflates **2**:**1** produced.

83 (15), 69 (40, $C_4H_6O^+$), 68 (100, $C_4H_5O^+$), 56 (44, $C_3H_{40}$).

Further products of solvolysis were analyzed by GC, NMR, GC/MS, comparison with an authentic sample, or hydrolysis to a known product. Pertinent analytical data for each product are given elsewhere in the Experimental Section.

**Cyclopentyl Methyl Ketone (21).** Cyclopentanecarboxylic acid[41] (50 g, 0.44 mol) was placed in a 2-L, 3-neck flask fitted with an $N_2$ inlet, drying tube, and separatory funnel, diluted with 400 mL of absolute ethyl ether, and cooled to −78 °C. Over the course of 1 h, 500 mL of a solution of 2 M methyllithium (in ether) was added dropwise. During the next 24 h the temperature was allowed to rise to 25 °C. Saturated $NH_4Cl$ solution (150 mL) was added; the ether phase was separated and washed thrice with 100 mL of $H_2O$. After drying over $CaCl_2$ and distillation 39.8 g (81%) of **21** was obtained: bp 85 °C (107 mbar); $^1$H NMR δ 1.67 (m, 8 H, methylene H, cyclopentane ring), 2.1 (s, 3 H, $CH_3$), 2.6–3.1 (m, 1 H, H-1, cyclopentane ring); IR (cm$^{-1}$) 1170 (C—C adjacent to C═O), 1190 (δ sym $CH_3$), 1370 (δ asym $CH_3$), 1720 (C═O); MS, *m/e* 112 (63%, $M^+$), 113 (7), 97 (20, $M^+ - CH_3$), 71 (85, $C_4H_7O^+$), 69 (100, $C_6H_9^+$), 67 (26), 43 (90, $CH_3CO^+$).

**Cyclopentylideneethyl Triflate (2).** Trifluoromethanesulfonic anhydride (6.1 g, 22 mmol) in 100 mL of methylene chloride was treated with 10 g (0.1 mol) of $Na_2CO_3$ and 2.4 g (20 mmol) **21** in 20 mL of methylene chloride. An isomeric mixture was obtained (78%, 3.81 g) containing **2** and 1-cyclopentylvinyl triflate (ratio 92:8). The triflate **2** was easily separated by preparative GC (3 m UCCW 982 at 1709): $^1$H NMR δ 1.6–1.9 (m, 4 H, methylene H; C-3, C-4), 2.05 (quint, 3 H, $CH_3$, $^5J$ = 1.7 Hz), 2.2–2.7 (m, 4 H, methylene H, C-2, C-5); IR (cm$^{-1}$) 925 (sym C—$OSO_2$), 960 (S—O), 1150 (sym S═O), 1220 (C—F), 1260 (asym C—$OSO_2$), 1395 (asym S═O), 1725 (C═C); MS, *m/e* 244 (92%, $M^+$), 245 (10), 246 (6), 111 (13, $M^+ - SO_2CF_3$), 96 (11, $M^+ - OSO_2CF_3$ + H), 95 (67, $M^+ - OSO_2CF_3$), 79 (40), 69 (81, $CF_3^+$), 68 (27, $C_5H_8^+$).

The spectra of cyclopentylvinyl triflate are as follows: $^1$H NMR δ 1.5–2.2 (m, 9 H, cyclopentyl H), 4.8–5.1 (m, 2 H, vinyl H); IR (cm$^{-1}$) 870 (sym C—$OSO_2$), 920 (S═O), 1130 (sym S═O), 1210 (C—F), 1420 (asym S═O), 1665 (C═C). The triflate **2** can also be prepared through the trimethylsilyl ether as described for **1**.

**Solvolysis of 2.** Solvolyses and product analyses were carried out as described for triflate **1**.

**Vinylidenecyclopentane (19):** $^1$H NMR δ 1.55–1.85 (m, 4 H, methylene H, C-3, C-4), 2.15–2.5 (m, 4 H, methylene H, C-2, C-5), 4.56 (quint 2 H, ═C═$CH_2$, $^5J$ = 4.5 Hz); IR (cm$^{-1}$) 850 (δC—H, ═C═$CH_2$), 1950 (═C═$CH_2$), 3050 (C—H, ═C═$CH_2$).

**Cyclopentylideneethyl Trifluoroethyl Ether (20):** $^1$H NMR δ 1.45–1.95 (m, 4 H, methylene H, C-3, C-4), 1.75 (quint, 3 H, $CH_3$, $^5J$ = 1.5 Hz), 1.8–2.5 (m, 4 H, methylene H, C-2, C-5), 3.95 (quart, 2 H, $OCH_2CF_3$, $^3J_{HF}$ = 8.5 Hz); IR (cm$^{-1}$) 860 (C—O), 975 (C—O), 1090 (C—O), 1170 (C—F), 1240, 1295, 1390, 1440, 1715 (C═C); MS, *m/e* 194 (62%, $M^+$), 179 (100, $M^+ - CH_3$), 166 (30, $M^+ - C_2H_5$), 127 (20), 113 (10), 95 (28, $M^+ - OCH_2CF_3$), 83 (14, $CH_2CF_3^+$), 71 (15), 79 (43).

**Hex-5-yn-1-ol.** The carbinol was prepared from 2-(chloromethyl)-tetrahydropyran[42] as described by Tufariello and Trybulski.[42] $^1$H NMR δ 1.45–1.9 (m, 4 H, methylene H, C-2, C-3), 1.75 (t, 1 H, H-C C-, $^4J$ = 2.4 Hz), 2.0–2.4 (m, 2 H, -C≡C-$CH_2$-), 3.64 (t, 2 H, -$CH_2$-O, *J* = 6 Hz), 3.83 (s, 1 H, OH); $^{13}$C NMR δ 18.20 (C-4), 24.96 (C-3), 31.65 (C-2), 61.42 (C-1), 69.16 (C-6), 84.23 (C-5); IR (cm$^{-1}$) 2140 (C≡C), 3350 (≡C-H), 3380 (O—H); MS, *m/e* 98 (1%, $M^+$), 99 (7), 97 (13, $M^+ - H$), 79 (69, $M^+ - H$, $M^+ - H_2O$), 70 (100, $M^+ - C_2H_4$), 67 (20), 53 (22), 39 (64).

**Hex-5-yn-1-yl Triflate (6).** This triflate was prepared by the general procedure[16,18,37] for triflates: $^1$H NMR δ 1.5–2.1 (m, 4 H, methylene H, C-2, C-3), 1.9 (t, 1 H, HC≡C, $^4J$ = 2.3 Hz), 2.1–2.5 (m, C≡C$CH_2$), 4.6 (t, 2 H, $CH_2$OTf, *J* = 6 Hz); IR (cm$^{-1}$) 940 (sym C—$OSO_2$), 1040 (S—O), 1150 (sym S═O), 1175, 1220 (C—F), 1250 (asym C—$OSO_2$), 1420 (asym S═O), 2160 (C≡C), 3350 (≡CH).

**Cyclohexenyl Triflate.** Cyclohexenyl triflate was prepared by the previously described procedure[40] (see procedure for preparation of **1**). An authentic sample was needed for comparison: $^1$H NMR δ 1.5—1.9 (m, 4 H, methylene H), 2.1—2.5 (m, 4 H, $CH_2$C═C), 5.75 (m, 1 H, vinyl H); IR (cm$^{-1}$) 840, 885, 985 (sym C-$OSO_2$), 1040 (S-O), 1060, 1082, 1150 (sym S═O), 1220 (C-F), 1250 (asym S═O), 1420 (asym S═O), 1680 (C═C); MS, *m/e* 230 (30%, $M^+$), 97 (13, $M^+ - SO_2CF_3$), 81 (15, $M^+ - OSO_2CF_3$), 79 (58, $C_6H_7^+$), 69 (62, $CF_3^+$), 54 (38, $C_4H_6^+$), 41 (100, $C_3H_5^+$).

**Solvolysis Products from Hex-5-yn-1-yl Triflate. (a) Hex-5-yn-1-yl trifluoroethyl ether:** $^1$H NMR δ 1.5–1.9 (m, 4 H, methylene H, C-2, C-3), 1.95 (t, 1 H, HC≡C, $^4J$ = 2.4 Hz), 2.1–2.5 (m, 2 H, C≡C$CH_2$), 3.6 (t, 2 H, $CH_2$O, *J* = 6 Hz), 3.8 (quart, 2 H, $OCH_2CF_3$, *J* = 8.8 Hz); IR (cm$^{-1}$) 975 (sym C—O), 1140, 1160 (C—F), 1280 (asym C—O), 1310, 2130 (C≡C), 3320 (≡C—H); MS, *m/e* 180 (3%, $M^+$), 179 (27, $M^+ - H$), 165 (42, $M^+ - H$, $M^+ - CH_2$), 152 (100, $- C_2H_4$), 139 (70, $- C_3H_5$), 113 (98, $- CH_2OCH_2CF_3$), 83 (42, $C_6H_{11}$), 81 (31, $- OCH_2CF_3$), 79 (94, $C_6H_7$).

**(b) Cyclohexenyl trifluoroethyl ether:** $^1$H NMR δ 1.4–1.9 (m, 4 H, methylene H, C-4, C-5), 1.9–2.4 (m, 4 H, methylene H, C-3, C-6), 3.94 (quart, 2 H, $OCH_2CF_3$, $^3J_{HF}$ = 8 Hz), 4.6 (m, 1 H, vinyl H); IR (cm$^{-1}$) 870, 980, 1170 (sym C—O), 1195 (C—F), 1295 (asym C—O), 1670 (C═C); MS, *m/e* 180 (100%, $M^+$), 179 (75, $M^+ - H$), 165 (73, $M^+ - H$, $M^+ - CH_2$), 152 (91, $M^+ - C_2H_4$), 113 (8, $CF_3CH_2OCH_2^+$), 83 (17, $C_6H_{11}^+$), 81 (22, $M^+ - OCH_2CF_3$), 79 (22, $C_6H_7^+$), 69 (7, $CF_3^+$).

**Hex-4-yn-1-ol.** Hex-5-yn-1-ol was isomerized to hex-4-yn-1-ol in alcoholic KOH. The yield was 51%. Better yields were obtained when, before the isomerization, the hydroxyl group was protected with the tetrahydropyran group by using dihydropyran.[43] The hex-5-yn-1-yl tetrahydropyranyl ether was then heated for 3 h in an autoclave at 170 °C with a like volume of 4 N alcoholic KOH. There was an 8-bar pressure buildup. The mixture was poured into water, extracted with ether and concentrated. Yield was 90%. Cleavage of the protecting group in methanol with a few drops of HCl yielded the hex-4-yn-1-ol: Workup and distillation yielded 80:; bp, 95 °C (40 mbar); $^1$H NMR δ 1.5–1.8 (m, 2 H, $CH_2CH_2OH$), 1.76 (t, 3 H, $CH_3$C≡C, $^5J$ = 2.5 Hz), 1.95–2.35 (m, 2 H, C≡C$CH_2$), 2.7 (s, 1 H, OH), 3.6 (t, 2 H, $CH_2$O, *J* = 6.2 Hz); $^{13}$C NMR 3.5 (C-6), 15.4 (C-3), 31.6 (C-2), 76.3 (C-5, 78.6 (C-4).

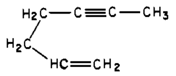
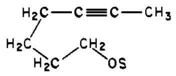
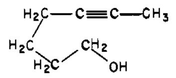
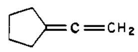
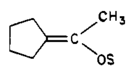
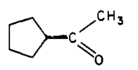
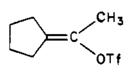
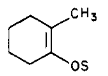
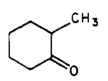
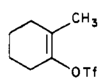
**Hex-4-yn-1-yl Triflate (7).** The synthesis was carried out as described for the preparation of **1**. Column chromatography (Kieselgel) with petroleum ether (30–40 °C) as eluent provided a colorless liquid: yield

(41) Zelinsky, N. *Ber. Dtsch. Chem. Ges.* **1908**, *41*, 2627.

(42) Tufariello, J. J.; Trybulski, E. J. *J. Org. Chem.* **1974**, *39*, 3378.

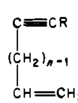
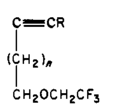
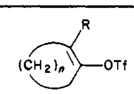
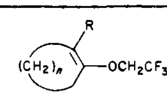
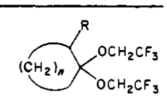
(43) Woods, G. F.; Kramer, D. N. *J. Am. Chem. Soc.* **1947**, *69*, 2246. van Boom, J. H.; van Boom, M. *Synthesis* **1973**, 169.

Table VII. Solvolyses of Hept-5-yn-1-yl Triflate (3): Variation of Product Ratio (Relative Percent) with Solvent (0 °C)

| products | | solvent (time, h) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 100% EtOH (11) | 80% EtOH (10) | $H_2O^a$ (9) | 80% TFE (9) | 97% TFE (6) | 100% TFE (6) | abs HFIP (6) | 100% $TFA^b$ (6) |
|  | (**16**) | 38 | 2 | <1 | <1 | <1 | <0.1 | 1 | <0.1 |
|  | (**17**) | 54 | 80 | | 8 | 3 | <0.1 | | |
|  | (**18**) | | 5 | 12 | 0.1 | | | | |
|  | (**19**) | | 3 | 1 | 2 | 1 | 1 | 1 | <1 |
|  | (**20**) | | | | 10 | 10 | 11 | 9 | |
|  | (**21**) | | 1 | 10 | 3 | 1 | <1 | <1 | 6 |
|  | (**2**) | | 2 | 50 | 68 | 74 | 80 | 82 | 90 |
|  | (**22**) | | | | 4 | 5 | 4 | 3 | |
|  | (**23**) | | <1 | 14 | 1 | <0.1 | <0.1 | 0.1 | 1 |
|  | (**1**) | | 1 | 6 | 2 | 3 | 3 | 3 | 2 |
| unidentified$^c$ | | 8/5 | 9/1 | 6/3 | 1/3 | | | 1/2 | 1/4 |
| $m_5/m_6$ | | | 4 | 3 | 12 | 11 | 18 | 17 | 32 |
| internal return$^d$ | | | | 8 | 34 | 25 | 27 | 27 | 45 |
| $m_{20+21}/m_{22+23}$ | | | | 3.0 | 2.7 | 2.6 | 3.2 | 3.5 | 6 |
| $k_\Delta/k_s$ | | 0.01 | 0.04 | 6 | 10 | 33 | 100 | 100 | 100 |

$^a$ Triflate 3 is sparingly soluble in water. $^b$ Buffer = $NaOOCCF_3$. Hydrolyzed with NaOH before analysis. $^c$ The values are %/no. of peaks. $^d$ See Table IX, footnote *b*.

Table VIII. Products of Solvolyses of the Alkynyl Triflates 6, 7, 8, and 9 in 100% TFE with $Na_2CO_3$ Buffer

| triflate | products, % | | | | | | |
|---|---|---|---|---|---|---|---|
| |  |  | |  |  | |  |
| $HC{\equiv}C(CH_2)_3OTf^a$ 6, R = H, *n* = 2 | 4 | 93 | $1^b$ | | | | |
| $CH_3C{\equiv}C(CH_2)_3OTf^c$ 7, R = $CH_3$, *n* = 2 | | 98 | $2^b$ | | | | |
| $HC{\equiv}C(CH_2)_4OTf^d$ 8, R = H, *n* = 3 | 4 | 58 | $<1^b$ | 12 | 24 | $1^b$ | 2 |
| $HC{\equiv}C(CH_2)_5OTf^e$ 9, R = H, *n* = 4 | 6 | 74 | $<1^b$ | 3 | 9 | $1^b$ | 2 |

$^a$ 60 °C, 17 days. $^b$ Hydrolyzed (to carbinol). $^c$ 60 °C, 24 h. $^d$ 0 °C, 2 days. $^e$ 0 °C, 2 days.

73%; $^1H$ NMR $\delta$ 1.7–2.1 (m, 2 H, $CH_2CH_2OTf$), 1.76 (t, 3 H, $CH_3$-$C{\equiv}C$, $^5J$ = 2.3 Hz), 2.1–2.6 (m, 2 H, $C{\equiv}CCH_2$), 4.6 (t, 2 H, $CH_2OTf$, $J$ = 6 Hz); IR (cm$^{-1}$) 935 (sym C—$OSO_2$), 1150 (sym S=O), 1215 (C—F), 1250 (asym C—$OSO_2$), 1420 (asym S=O).

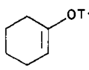
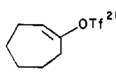
**Solvolysis Products from 7. Hex-4-yn-1-yl trifluoroethyl ether:** $^1H$ NMR $\delta$ 1.5–2.0 (m, 2 H, $CH_2CH_2O$), 1.8 (t, 3 H, $CH_3C{\equiv}C$, $^5J$ = 2.3 Hz), 2.0–2.3 (m, 2 H, $C{\equiv}CCH_2$), 3.65 (t, 2 H, $CH_2OTf$, $J$ = 6 Hz), 3.69 (quart, 2 H, $OCH_2CF_3$, $^3J$ = 9 Hz).

**5-Chloropentyl Tetrahydropyranyl Ether.** The carbinol was prepared from 5-chloropentyl acetate[44] (250 g, 1.5 mol) by treatment at room temperature with 1 L of ethanol and 1 L of 2 N NaOH. After 12 h the ethanol was distilled, the organic phase was removed, and the aqueous phase was well washed with benzene. The combined organic phases were dried by distillation of the benzene azeotrope: yield 183 g (98%); bp, 73 °C (13 mbar). The alcohol was converted to 5-chloropentyl tetrahydropyranyl ether by treatment with an equivalent amount of dihydropyran[43] at 10 °C with *p*-toluenesulfonic acid as the catalyst: bp 86–87 °C (0.7 mbar); yield 85%.

**Hept-6-yn-1-ol.** 5-chloropentyl tetrahydropyranyl ether (103 g, 0.5 mol) was dissolved in 100 mL of HMPT and added slowly at 0 °C to a mixture of 48 g (1 mol) of sodium acetylide in 200 mL of THF and 100 mL of HMPT ($N_2$ atmosphere, stirrer, separatory funnel, and drying tube). The mixture was stirred 12 h and poured into 1 L of an ice–water mixture. $NH_4Cl$ (50 g) was added, and then, slowly dilute HCl was added until the color turned yellow. After extraction with ether the

(44) Synenholm, M. E. *J. Am. Chem. Soc.* **1947**, *69*, 2581.

Table IX. Kinetics of the Solvolyses of Triflates **8**, **10**, **9**, and **24**[21]

| triflate | solvent | temp, °C | $k$, $s^{-1}$ | EA, kJ/mol | $\Delta H^{\ddagger}$, [kJ/mol] | $\Delta S^{\ddagger}$, J/mol |
|---|---|---|---|---|---|---|
| HC≡C$(CH_2)_4$OTf **8** | 97% TFE | 30.0 | $1.98 \pm 0.02 \times 10^{-4}$ | 92 | 90 | −20 |
| | | 50.0 | $1.9 \pm 0.2 \times 10^{-3}$ | | | |
|  **10** | 50% EtOH | 100.0 | $5.47 \times 10^{-7}$ | | 130 | −17.2 |
| | | 125.2 | $8.16 \pm 0.16 \times 10^{-6}$ | | | |
| | 60% EtOH | 100.0 | $2.15 \times 10^{-7}$ | | 134 | −15.9 |
| | | | $4.10 \pm 0.15 \times 10^{-5}$ | | | |
| HC≡C$(CH_2)_5$OTf **9** | 97% TFE | 30.0 | $1.18 \pm 0.04 \times 10^{-4}$ | 73 | 71 | |
| | | 50.0 | $7.1 \pm 0.2 \times 10^{-4}$ | | | |
| | 80% TFE | 30.0 | $1.08 \pm 0.04 \times 10^{-3}$ | | | |
|  **24** | 97% TFE | 75.3 | $1.07 \pm 0.01 \times 10^{-5}$ | | 97 | −62.4 |
| | | 99.8 | $1.08 \pm 0.01 \times 10^{-4}$ | | | |
| | 70% TFE | 75.2 | $3.39 \pm 0.04 \times 10^{-5}$ | | 113.0 | −8.0 |
| | | 100.7 | $5.07 \pm 0.03 \times 10^{-4}$ | | | |

organic phase was washed with saturated $NH_4Cl$ solution, dried over $MgSO_4$, and distilled: bp, 94 °C (0.07 mbar); yield, 83 g (85%). The crude product was used for further syntheses. Hept-6-yn-1-ol was obtained from the ether by acid catalysis: bp, 85 °C (2 mbar); yield 98%; $^1$H NMR δ 1.4–1.7 (m, 6 H, methylene H, C-2, 3, 4), 1.83 (t, 1 H, HC≡C, $^4J$ = 2.5 Hz), 2.0–2.3 (m, 2 H, C≡$CCH_2$), 3.5 (t, 2 H, $CH_2O$, $J$ = 6 Hz), 4.05 (s, 1 H, OH); $^{13}$C NMR δ 18.46 (C-5), 25.22 (C-4), 28.53 (C-3), 32.17 (C-2), 61.94 (C-1), 69.03 (C-7), 84.23 (C-6); IR ($cm^{-1}$) 1050, 1260, 2140 (C≡C), 3360 (≡C—H), 3370 (OH); MS, $m/e$ 112 (0.7%, $M^+$), 97 (20, $M^+$ − H, $M^+$ − $CH_2$), 39 (13, $M^+$ − H, $M^+$ − $H_2O$), 84 (30, $M^+$ − $C_2H_4$), 83 (16, $M^+$ − $C_2H_5$).

**Hept-6-yn-1-yl Triflate (9).** Triflate **9** was prepared from hept-6-yn-1-ol exactly as described for triflates **6** and **8**. Since triflate **9** is quite unstable, it must be freshly prepared before each solvolysis and used immediately without any further purification. $^1$H NMR δ 1.5–2.0 (m, 6 H, methylene H, C-2, C-3, C-4), 1.7 (t, 1 H, HC≡C, $^4J$ = 2.5 Hz), 2.0–2.4 (m, 2 H, C≡$CCH_2$), 4.5 (t, 2 H, $CH_2$OTf, $J$ = 6 Hz); IR ($cm^{-1}$) 850, 950 (S—O), 1080 (sym C—$OSO_2$), 1160 (sym S=O), 1225 (C—F), 1260 (asym C—$OSO_2$), 1430 (asym S=O), 2150 (C≡C), 3360 (≡C—H).

**Cycloheptenyl Triflate (24).** Cycloheptenyl triflate was prepared from cycloheptanone as described for the synthesis of **1**. It was synthesized for use as an authentic sample for comparison purposes. IR ($cm^{-1}$) 875 (S—O), 955, 1000 (S—O), 1150 (sym C—$OSO_2$), 1225 (C—F), 1260 (asym C—$OSO_2$), 1430 (asym S=O), 1695 (C=C); MS, $m/e$ 244 (90%, $M^+$), 246 (5), 245 (9), 111 (9, $M^+$ − $SO_2CF_3$), 95 (32, $M^+$ − $OSO_2CF_3$), 94 (75), 83 (52), 79 (71).

**Solvolysis Products from Hept-6-yn-1-yl Triflate (9). (a) Hept-6-yn-1-yl trifluoroethyl ether:** $^1$H NMR δ 1.4–2.1 (m, 6 H, methylene H, C-2, C-3, C-4), 1.8 (t, 1 H, HC≡C, $^4J$ = 2.5 Hz), 2.0–2.4 (m, 2 H, C≡$CCH_2$), 3.6 (t, 2 H, $CH_2O$, $J$ = 6 Hz), 3.8 (quart, 2 H, $OCH_2CF_3$, $^3J_{HF}$ = 9 Hz); IR ($cm^{-1}$) 985 (S—O), 1140 (sym C—O), 1165 (C—F), 1280 (asym C—O), 2130 (C≡C), 3320 (≡C–H); MS, $m/e$ 194 (1%, $M^+$), 179 (20, $M^+$ − H, $M^+$ − $CH_2$), 155 (4, $M^+$ − $CH_2C$≡CH), 159 (29, $M^+$ − $C_3H_6$), 139 (28), 113 (100, $M^+$ − $CH_2OCH_2CF_3$), 93 (18), 83 (27, $CF_3CH_2^+$), 81 (40, HC≡C$(CH_2)_4^+$), 79 (98), 67 (35, HC≡C$(CH_2)_3^+$).

**(b) Cycloheptenyl trifluoroethyl ether:** $^1$H NMR δ 1.4–1.9 (m, 6 H, methylene H, C-3, C-4, C-5), 1.9–2.2 (m, 2 H, methylene H, C-3), 2.2–2.5 (m, 2 H, methylene H, C-7), 3.86 (quart, 2 H, $OCH_2CF_3$, $^3J_{HF}$ = 8 Hz), 4.65 (m, 1 H, vinyl H); IR ($cm^{-1}$) 865, 980, 1140 (sym C—O), 1170 (C—F), 1290 (asym C—O), 1660 (C=C); MS, $m/e$ 194 (97%, $M^+$), 179 (100, $M^+$ − H, $M^+$ − $CH_2$), 166 (70, $M^+$ − $C_2H_4$), 165 (99, $M^+$ − $C_2H_5$), 94 (23, $M^+$ − $HOCH_2CF_3$).

**(c) Cycloheptenyl Triflate.** The data for this solvolysis product are in complete agreement with the data (vide supra) given for the authentic sample.

**Hept-5-yn-1-yl Triflate (3).** Hept-5-yn-1-ol was prepared by the isomerization of hept-6-yn-1-ol exactly as described (vide supra) for the preparation of hex-4-yn-1-ol. In contrast to the (by one methylene group) lower homologue, the THP protecting group is not necessary; bp, 70–73 °C (7 mbar); yield 98%; $^1$H NMR δ 1.4–1.8 (m, 4 H, methylene H, C-3, C-4), 1.76 (t, 3 H, $CH_3C$≡C, $^5J$ = 2.5 Hz), 1.9–2.3 (m, 2 H, C≡$CCH_2$), 2.85 (s, 1 H, OH), 3.6 (t, 2 H, $CH_2O$, $J$ = 6 Hz); $^{13}$C NMR δ 3.2 (C-7), 18.9 (C-4), 26.1 (C-3), 32.2 (C-2), 62.0 (C-1), 75.9 (C-6), 79.4 (C-5); IR ($cm^{-1}$) 3420 (O–H); MS, $m/e$ 112 (6%, $M^+$), 98 (20, $M^+$ − $CH_3$), 94 (7, $M^+$ − $H_2O$), 92 (14), 85 (44, $M^+$ − $C_2H_3$), 84 (18, $M^+$ − $C_2H_4$), 80 (53, $M^+$ − $CH_2OH_2^+$), 69 (100, $M^+$ − $CH_3CO$).

The carbinol was converted to hept-5-yn-1-yl triflate (**3**) as described above.[16,18,37] The triflate **3** is unstable, but can be prepared using Freon-11 as a solvent. Temperatures above 0 °C must be avoided. The triflate (**3**) may be preserved for short periods in liquid nitrogen, but repeated melting and freezing should also be avoided. $^1$H NMR (Freon-11) δ 1.55–2.1 (m, 4 H, methylene H, C-2, C-3), 1.73 (t, 3 H, $CH_3C$≡C, $^5J$ = 2.4 Hz), 2.1–2.4 (m, 2 H, C≡$CCH_2$), 455 (t, 2 H, $CH_2$OTf, $J$ = 6 Hz); IR ($cm^{-1}$) 850, 940 (sym $COSO_2$), 1075 (S–O), 1155 (sym S=O), 1105, 1220 (C–F), 1260 (asym $COSO_2$), 1430 (asym S=O).

**Hept-5-yn-1-yl Trifluoroethyl Ether (17).** Ether **17** was needed as an authentic sample for comparison purposes. It was prepared according to the procedure of Beard, Baum, and Grakansas:[45] $^1$H NMR δ 1.5–1.85 (m, 4 H, methylene H, C-2, C-3), 1.73 (t, 3 H, $CH_3C$≡C, $J$ = 2.4 Hz), 1.9–2.3 (m, 2 H, C≡$CCH_2$), 3.6 (t, 2 H, $CH_2O$, $J$ = 6 Hz); IR ($cm^{-1}$) 870, 980, 1150 (sym C–O), 1170 (C–F), 1220, 260, 1290 (asym C–O).

**Hept-1-en-5-yn (16).**[46] Compound **16** was prepared from 1,2-dibromo-5-hexene[47] by the procedure of Huntsman, Boer, and Woosley.[46] Sodium amide (from 8 g of Na in 200 mL of liquid ammonia) was treated dropwise with 1,2-dibromo-5-hexene. The reaction was stirred 1 h (−60 °C), and over the next 45 min 22 g (0.15 mol) of methyl iodide was added to the mixture. After an additional 2 h, 11 g (0.2 mol) of $NH_4Cl$ and finally 100 mL of ether were added. The ammonia was allowed to evaporate, the resulting mixture was treated cautiously with water, and the organic phase was separated and washed with 5% aqueous $H_2SO_4$, water, and $NaHCO_3$ solution. After being dried and distilled (42% yield) the crude product was purified by preparative GC. The yield of **16** was 35%. $^1$H NMR δ 1.75 (t, 3 H, $CH_3C$≡C, $^5J$ = 2.2 Hz), 2.2–2.35 (m, 4 H, methylene H), 4.85–5.0 (m, 1 H, vinyl H (cis)), 5.0–5.3 (m, 1 H, vinyl H (trans)), 5.5–6.2 (m, 1 H, vinyl H); IR ($cm^{-1}$) 920 (δC=$CH_2$), 1000 (δHC=CH trans), 1650 (C=C), 1850 (2νC=C), 2080 (C≡C), 3020 (=CHR), 3110 (=$CH_2$).

**Solvolysis Products from 3.** The retention times of the solvolysis products **16** and **17** were identical with those of authentic samples, which had been prepared for comparison purposes. Mixtures of authentic and solvolysis product were also injected and proved to be homogeneous. The spectroscopic data for the remaining solvolysis products are given elsewhere in this article.

**Acknowledgment.** C.J.C. thanks the Alexander von Humboldt-Stiftung for its generous support of portions of this work through a Senior U.S. Scientist award.

**Registry No. 1**, 32363-21-6; **2**, 85355-17-5; **3**, 85355-18-6; **6**, 85355-19-7; **7**, 85355-20-0; **8**, 85355-21-1; **9**, 85355-22-2; **10**, 28075-50-5; **16**, 821-40-9; **17**, 85355-23-3; **18**, 58944-42-6; **19**, 7439-00-1; **20**, 85355-24-4; **21**, 6004-60-0; **22**, 85355-25-5; **23**, 583-60-8; **24**, 28075-51-6; 3-methylcyclohexenyl triflate, 76605-82-8; chlorotrimethylsilane, 75-77-4; 6-methylcyclohexenyl trimethylsilyl ether, 19980-33-7; cyclopentanecarboxylic acid, 3400-45-1; methyllithium, 917-54-4; trifluoromethanesulfonic anhydride, 358-23-6; hex-5-yn-1-ol, 928-90-5; 2-(chloro-

(45) Beard, C. D.; Baum, K.; Grakansas, V. *J. Org. Chem.* **1973**, *38*, 3673.
(46) Huntsman, W. D.; Boer, J. A.; Woosley, M. H. *J. Am. Chem. Soc.* **1966**, *88*, 5846.
(47) Sondheimer, F.; Ben-Efraim, D. A.; Wolovsky, R. *J. Am. Chem. Soc.* **1961**, *83*, 1675.

methyl)tetrahydropyran, 18420-41-2; cyclohexenyl trifluoroethyl ether, 85355-26-6; hex-5-yn-1-yl tetrahydropyranyl ether, 1720-37-2; hex-4-yn-1-yl trifluoroethyl ether, 85355-27-7; 5-chloro-1-pentanol, 5259-98-3; 5-chloropentyl acetate, 20395-28-2; 5-chloropentyl tetrahydropyranyl ether, 13129-60-7; dihydropyran, 110-87-2; hept-1-yn-1-ol, 63478-76-2; sodium acetylide, 2881-62-1; cycloheptanone, 502-42-1; hept-6-yn-1-yl trifluoroethyl ether, 85355-28-8; cycloheptenyl trifluoroethyl ether, 85355-29-9; 1,2-dibromo-5-hexene, 4285-48-7; hex-4-yn-1-yl tetrahydropyranyl ether, 85355-30-2; hex-4-yn-1-ol, 928-93-8; 2-methylcyclohexenyl trimethylsilyl ether, 19980-35-9.

# 1-Benzyl-1,4-dihydronicotinamide as a Reagent for Replacing Aliphatic Nitro Groups by Hydrogen. An Electron-Transfer Chain Reaction[1]

**Noboru Ono,* Rui Tamura, and Aritsune Kaji***

*Contribution from the Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606, Japan.* *Received August 11, 1982*

**Abstract:** The reaction of $\alpha$-nitro nitriles, $\alpha$-nitro esters, and $\alpha$-nitro ketones with 1-benzyl-1,4-dihydronicotinamide (BNAH) can occur with selective replacement of the nitro group by hydrogen without affecting other functional groups. Evidence is presented to support the claim that the reaction proceeds via an electron-transfer chain mechanism in which radical anions and free radicals are intermediates.

1-Benzyl-1,4-dihydronicotinamide (BNAH) is of interest as a model of the biochemistry important reduced nicotinamide–adenine dinucleotide phosphate [NAD(P)H] and, also, because it has been shown to reduce a very wide variety of organic compounds.[2] Most of these reductions are believed to proceed by a direct hydride-transfer mechanism,[3] but recently some reductions have been proposed which proceed via electron-transfer mechanism[4] (transfer of an electron and a hydrogen, or transfer of two electrons and a proton in three steps). We now present a new reaction of BNAH: the replacement of an aliphatic nitro group by hydrogen, which proceeds as an electron-transfer chain reaction. Reduction of organic nitro compounds with BNAH was first reported in 1962 by Dittmer and Kolyer.[5] Since then there have been no reports concerning the reduction of nitro compounds by 1,4-dihydropyridines. Recent interest in the electron-transfer reaction of nitro compounds[6] and in the mechanism of the reduction by 1,4-dihydropyridines led us to study the reaction of aliphatic nitro compounds with BNAH.[1]

(1) Abstracted from the Ph.D. dissertation of R. T. Kyoto, 1980. Preliminary communication: N. Ono, R. Tamura, and A. Kaji, *J. Am. Chem. Soc.*, **102**, 2851 (1980).

(2) Various unsaturated compounds such as C=O, C=S, or $C=N^+$ are reduced by BNAH or related compounds, which is well documented in D. M. Stout and A. T. Meyers, *Chem. Rev.*, **82**, 223 (1982).

(3) (a) H. Sund in "Biological Oxidation", T. P. Singer, Ed., Wiley-Interscience, New York, 1968, pp 621–624; (b) D. J. Creigton and D. S. Sigman, *J. Am. Chem. Soc.*, **93**, 6314 (1971); (c) D S Sigman, J. Hadiu, and D. J. Creigton, *Bioorg. Chem.*, **4**, 385 (1978); (d) I. MacInnes, D. C. Nonhebel, S. T. Orszulik, and C. J. Sukling, *J. Chem. Soc., Chem. Commun.*, 121 (1982); (e) J. W. Bunting and S. Sindhuatmadia, *J. Org. Chem.*, **46**, 4211 (1981); J. M. Bunting, V. S. F. *Chew*, and G. Chu, *ibid.* **47**, 2303 (1982).

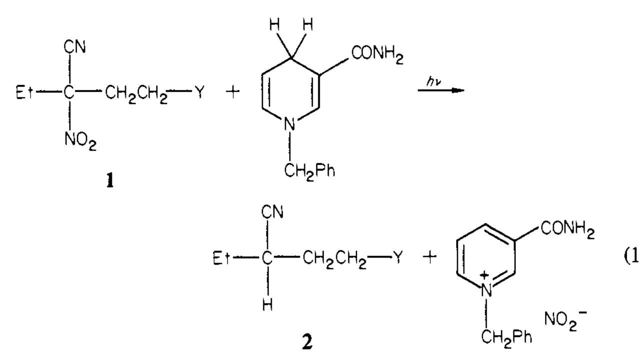
(4) (a) A. Ohno and N. Kito, *Chem. Lett.*, 369 (1972); (b) T. Okamoto, A. Ohno, and S. Oka, *J. Chem. Soc., Chem. Commun.*, 300 (1978); (c) A. Ohno, H. Yamamoto, and S. Oka, *J. Am. Chem. Soc.*, **103**, 2041 (1981); (d) A. Ohno, T. Shio, H. Yamamoto, and S. Oka, *ibid.* **103**, 2045 (1981); (e) S. Sinkai, T. Tsuno, and O. Manabe, *J. Chem. Soc., Chem. Commun.* 592 (1982); (f) T. Endo and M. Okawara, *J. Org. Chem.*, **45**, 2663 (1980); (g) R. J. Kill and D. A. Widdowson, *Bioorg. Chem.*, **4**, 239 (1978). Considerable confusion still exists in the reduction mechanism by 1,4-dihydropyridine derivatives. For example, the reduction of isoquinolinium cations is claimed to proceed via one-step hydride transfer mechanism;[3e] on the other hand, the reduction of *N*-methylacridinum cation is claimed to proceed via an electron–proton–electron transfer mechanism[4d] Both conclusions are derived from the same experiments: kinetic isotope effect and substituent effect.

(5) D. C. Dittmer and J. M. Kolyer, *J. Org. Chem.*, **27**, 56 (1962).

(6) (a) N. Kornblum, *Angew. Chem., Int. Ed. Engl.*, **14**, 734 (1975); (b) N. Kornblum, S. D. Boyd, and F. W. Stuchal, *J. Am. Chem. Soc.*, **92**, 5783 (1980); (c) N. Kornblum and A. S. Erickson, *J. Org. Chem.*, **46**, 1037 (1981); (d) G. A. Russel, B. Mudryk, H. Jawdosiuk, and Z. wrobal, *ibid.*, **47**, 1879 (1982); (e) N. Ono, R. Tamura, T. Nakatsuka, J. Hayami, and A. Kaji, *Bull. Chem. Soc. Jpn.*, **53**, 3295 (1980); (f) R. K. Norris and R. J. Symth-King, *Tetrahedron*, 1051 (1982).

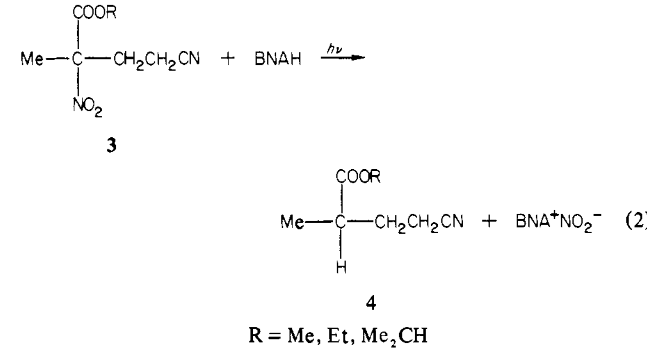
## Results and Discussion

Simple nitroalkanes such as *tert*-nitrobutane or 2-nitropropane cannot be reduced by BNAH as reported previously.[5] However, nitro compounds substituted with a cyano, carboalkoxy, or keto group at the $\alpha$ position were reduced by BNAH to the corresponding denitrated compounds. For example, the reaction of 3-cyano-3-nitroheptan-6-one (**1a**) with BNAH proceeded smoothly under irradiation of a 150-W tungsten lamp to give 3-cyanoheptan-2-one (**2a**) in 60% isolated yield; the pyridinium salt was isolated in 58% yield. In the dark, the starting material (**1a**) was recovered completely unchanged. Results of the conversion of $\alpha$-nitro nitriles (**1**) to the denitrated compounds (**2**) are summarized in Table III of the Experimental Section.



Y = C(=O)Me, COOMe, CN

In the same way, the nitro group of $\alpha$-nitro esters (**3**) was replaced by hydrogen under irradiation of a 150-W tungsten lamp (eq 2). The methyl ester (**3**) was reduced readily in benzene to



R = Me, Et, $Me_2CH$

0002-7863/83/1505-4017$01.50/0 