and the external bond angles; i.e., by deviation from planarity the external bond angles decrease and get closer to an ideal value simultaneously with pyramidalization of the double bond. Accordingly, the external bond angles found in the anti-endo-anhydride **3** with a planar double bond [143.4 (2)° and 144.1 (2)°][7] are similar to, whereas those in the puckered anti-exo-imide **4** [141.9 (2)° and 142.7 (2)°][9] differ significantly from, the value we have determined for *anti*-sesquinorbornene (**2**).

Finally, it would be tempting to compare our experimentally determined structure of *anti*-sesquinorbornene (**2**) with structures obtained by different theoretical methods. Unfortunately, the molecular mechanics methods tend to overestimate the relative stability of the puckered form relative to the one with a planar double bond by 1.7–1.8[10,12] and 8.1 kcal/mol[11] for Allinger's (MM2) force field[19] and Ermer's consistent force field,[11] respectively. Although Houk et al.[15] have suggested one way to overcome this problem by altering some of the original parameters, we feel that more work is needed on the force field approach before a detailed comparison of the experimental and calculated structures of *anti*-sesquinorbornene (**2**) is justified.

Experimental Section

anti-Sesquinorbornene **2** was prepared as described by Kopecky and Miller[20] and by Bartlett et al.[6e]

105 K Study. The crystals belong to the monoclinic system, space group $P2_1/n$, with $a = 6.112$ (2) Å, $b = 7.395$ (2) Å, $c = 9.850$ (3) Å, $\beta = 99.21$ (3)°, and $d_{calcd} = 1.211$ g cm^{-3} for $Z = 2$ (molecular formula $C_{12}H_{16}$), implying that the molecule possesses a crystallographic center of symmetry. The reflection data were collected on a PICKER-FACS1 diffractometer at the University of Copenhagen, using monochromatic Mo Kα radiation, scantype $\omega/2\theta$. The size of the crystal used in data collection was ca. 0.15 × 0.15 × 0.25 mm. A total of 4693 reflections were measured, $\theta \leq 35°$. The intensities were corrected for decay (approximately $0.02I$), Lorentz, and polarization effects but not for absorption ($\mu = 0.628$ cm^{-1}). Averaging of the symmetry-related reflections gave 1924 independent observations (internal R value on intensities, 1.8%); of these, 1475 were considered observed $[I > 3\sigma(I)]$ and used for structure analysis. The structure was solved by using the program SIMPEL[21] and refined by using the full-matrix least-squares program of the SDP package,[22] minimizing $\sum w(|F_o| - k|F_c|)^2$ with $w^{-1} = \sigma^2(F_o) + (p4)F_o^2$, $p = 0.07$, with the weighting scheme chosen to make $w\Delta F^2$ uniformly distributed in $|F|$. Atomic scattering factors for carbon were taken from Cromer and Mann,[23] while those for hydrogen were taken from Stewart, Davidson, and Simpson.[24] In the final cycle 87 parameters were refined by using anisotropic thermal parameters for the carbon atoms and isotropic thermal parameters for the hydrogen atoms. The final residuals are $R = 3.4\%$ and $R_w = 5.0\%$, $s = 1.17$. The final difference Fourier summation revealed a rather large peak (0.5 eÅ^{-3}) at the origin, which is the center of the double bond. All other peaks above 0.15 eÅ^{-3} could be assigned to bond regions.

243 K Study. The reflection data were collected on a crystal of dimensions 0.45 × 0.30 × 0.18 mm on a Syntex P2$_1$ diffractometer (along c axis) at Texas Christian University, using a $\theta/2\theta$ scan, $2\theta_{max} = 50°$, and graphite monochromated Mo Kα radiation. Lattice parameters were obtained by a least-squares refinement of 15 reflections (6.91° < 2θ < 15.86°) with the angles measured by a centering routine associated with the diffractometer. Systematic absences were consistent with space group $P2_1/n$. A total of 733 independent reflections were collected (equivalent reflections were averaged), and 641 had intensities greater than $3\sigma(I)$. Lorentz and polarization corrections were applied but no absorption corrections were made. Application of the direct methods program MULTAN78[25] revealed the positions of all carbon atoms. Hydrogen atom positions were located in subsequent difference Fourier syntheses. A full-matrix least-squares refinement, $\sum w(|F_o| - k|F_c|)^2$ minimized with $w = 1/\sigma^2(F_o)$ from counting statistics, yielded $R = 0.060$, $R_w = 0.069$, $(\Delta/\sigma)_{avg} = 0.019$, $(\Delta/\sigma)_{max} = 0.075$, and $S = 3.09$. The largest peak in the final difference Fourier map was 0.20 eÅ^{-3}. The calculations were performed with XRAY76.[26] Atomic scattering factors for carbon were taken from Cromer and Mann,[23] while those for hydrogen were taken from Stewart, Davidson, and Simpson.[24]

Acknowledgment. We are grateful to the Danish Natural Science Research Council for financial support and to Flemming Hansen (University of Copenhagen) for technical assistance.

Registry No. 2, 73679-39-7.

Supplementary Material Available: Tables listing anisotropic thermal parameters (105 K), bond lengths and bond angles (105 K), cell parameters (243 K), final position parameters (243 K), thermal parameters (243 K), bond lengths and bond angles (243 K), and a stereoscopic view of the crystal packing (105 K) (7 pages). Structure factor tables are available from the authors (M.G. or W.H.W.). Ordering information is given on any current masthead page.

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Remote Deuterium Isotope Effects in the Solvolysis of Ethynyl- and Butadiynylvinyl Triflates

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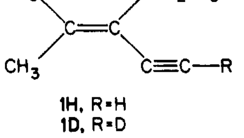
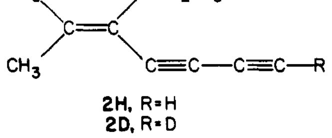
There are few cases where the remote secondary deuterium effect involving an alkynyl group has been examined. The isotope effect upon deuterium substitution in the 1-position of 3-chloro-3-methyl-1-butyne was reported[1] to be $k_H/k_D = 1.00 \pm 0.04$. To our knowledge, the only other examples of a remote deuterium effect involving an alkynyl group were observed in the solvolysis of **1** and **2**.[2,3]



1H, R=H
1D, R=D



2H, R=H
2D, R=D

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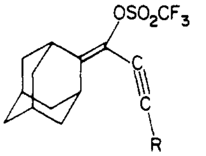
Table I. Rates of Solvolysis, Secondary Isotope Effects, and Solvent *m* Values for Ethynyl- and Butadiynylvinyl Triflates

compd	T, °C	solvent[a]	10^5k, s^{-1}	k_H/k_D[b]	$\Delta\Delta G^{\ddagger}$, cal mol^{-1}	m_{OTs}	m_{Cl}
3H	75.2 ± 0.2	60E	31.94 ± 0.1	1.036 ± 0.009	24.5		
	75.5 ± 0.2	70E	15.83 ± 0.2	1.051 ± 0.010	34.5	0.70	0.56
	75.5 ± 0.2	80E	7.36 ± 0.04	1.008 ± 0.007	5.5		
	75.5 ± 0.2	90E	2.911 ± 0.002	1.010 ± 0.010	6.9		
	65.4 ± 0.1	97T	16.38 ± 0.14	1.100 ± 0.012	64.5		
3D	75.5 ± 0.2	60E	30.82 ± 0.04[c]			0.68	0.55
	75.5 ± 0.2	70E	15.06 ± 0.2[c]				
	75.5 ± 0.2	80E	7.30 ± 0.03[c]				
	75.5 ± 0.2	90E	2.88 ± 0.01[c]				
	65.4 ± 0.1	97T	14.89 ± 0.05[c]				
5H	65.5 ± 0.1	70E	43.37 ± 0.07	1.321 ± 0.020	187.3		
	65.5 ± 0.1	80E	23.15 ± 0.10	1.264 ± 0.003	157.7	0.60	0.47
	65.5 ± 0.1	90E	10.14 ± 0.02	1.204 ± 0.010	124.9		
	35.4 ± 0.1	97T	18.47 ± 0.20	0.967 ± 0.004	-20.6		
5D	65.5 ± 0.1	70E	32.84 ± 0.08[d]				
	65.5 ± 0.1	80E	18.31 ± 0.04[d]			0.56	0.44
	65.5 ± 0.1	90E	8.42 ± 0.09[d]				
	35.4 ± 0.1	97T	19.10 ± 0.30[d]				

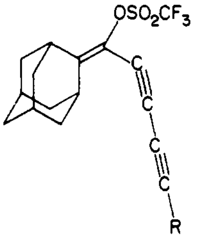
[a] 50E = 50:50 (v/v) ethanol/water; 60E, 70E, 80E, 90E similarly; 97T = 97:3 (w/w) 2,2,2-trifluoroethanol/water. [b] Corrected to 100% deuteration. [c] Uncorrected; material is 96.2% d_1 by mass spectral analysis. [d] Uncorrected; material is 91.6% d_1 by mass spectral analysis.

Both triflates show almost the same isotope effect, 1.05 and 0.94 in 60% EtOH and 97% TFE, respectively, and represent the first precise measurement of a deuterium isotope effect transmitted through an alkynyl moiety.

In order to provide further insight into these unique remote isotope effects we prepared and examined the solvolytic behavior of vinyl triflates **3** and **5** from the corresponding trimethylsilyl compounds **4** and **6**, respectively.



3H, R=H
3D, R=D
4, R=SiMe$_3$



5H, R=H
5D, R=D
6, R=SiMe$_3$

Results and Discussion

The rates of solvolyses of vinyl triflates **3H**, **3D**, **5H**, and **5D** were measured in buffered aqueous ethanol and TFE with triplicate paired (H,D) runs by using a precise conductometric technique (see Experimental Section). First-order rates of high precision were obtained in all instances to greater than 90% reaction. The rate constants, solvent *m* values, and the secondary deuterium isotope effects are summarized in Table I. The values are consistent with the direct unimolecular generation of the respective intermediate vinyl cation.[4]

The observed isotope effects, however, show a broad spectrum of values, with significant dependence on the solvent (which may indicate subtle mechanistic variations) and the type of acetylenic compound. The effect of a remote deuterium substitution on solvolytic reaction rates is normally small and inverse or unity.[2] The origin of such effects is attributed typically to an inductive effect of the isotopic atom.[2b] However, in the present case the observation of a "normal" isotope effect in aqueous ethanol implies an origin other than an inductive effect. Especially noteworthy are the unusually large isotope effects for the compounds **5H/5D** in aqueous ethanol, which are seen to be as high as 1.32. The presence of a "primary" component with ethanol abstracting hydrogen or deuterium from acetylenic carbon yielding the anion/carbene may explain these values. This suggestion is well-supported by earlier investigations of alkynylvinyl substrates, where equilibrium formation of the corresponding anion was indicated by the rapid exchange of the alkynyl proton in deuterated media.[5]

A marked reduction of isotope effect was observed[3] for the solvolyses of triflates **1H/1D** and **2H/2D** in 97% TFE compared to aqueous EtOH (k_H/k_D = 0.94 vs. 1.05), implying nucleophilic involvement of the solvent is significant in the transition state. In solvents of low nucleophilicity external attack by solvent at the terminal alkynyl or diynyl group in a tight ion pair may become rate limiting. A similar scheme has been proposed by Shiner and coworkers in the solvolysis of cyclopentyl brosylate.[6]

Total rehybridization (sp → sp^2) at the terminal position should[7] result in a maximum isotope effect of k_H/k_D = 0.78, placing the observed value of 0.95 well within the expected region for incomplete rehybridization owing to some nucleophilic attachment at the transition state. Similar nucleophilic involvement of solvent is possible in the solvolyses of triflates **5H/5D** in 97% TFE. In contrast, in the solvolyses of triflates **3H/3D** in 97% TFE a normal isotope effect (k_H/k_D = 1.10) is obtained. In these esters the approach of solvent to the acetylenic carbon may be hindered by the bridgehead hydrogens and the triflate group which are within the path of solvent approach. Consequently the degree of sp → sp^2 rehybridization is drastically diminished, resulting in a "normal" remote deuterium isotope effect. Product studies which might provide further support for our explanation of these unique isotope effects are not feasible in these extremely labile systems.

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In summary, we have provided evidence for unique remote kinetic deuterium isotope effects of considerable variation in solvolytic systems. These values represent the largest and most remote secondary kinetic isotope effects reported to date. The unexpectedly large effects of 1.32 in the case of butadiynyl system **5** may involve a primary component whereas the expected inverse effects in 97% TFE are consistent with a rehybridization at the terminal center. The larger magnitude of remote isotope effects in these vinylic systems compared to saturated substrates is due to the greater need for stabilization of vinyl cations compared to saturated carbocations.[4]

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 298 spectrometer. Deuterium content was determined on a Varian MAT GC-mass spectrometer. Solvents and reagents were purified and dried by standard procedures immediately prior to use. Vinyl triflates **3H**[8] and **5H**[9] were prepared and characterized as previously described.

Vinyl triflate 3D was prepared from the corresponding (trimethylsilyl)vinyl triflate (**4**) in a manner similar to the nondeuterated analogue.[3,8] This procedure gave **3D** as a colorless oil with a deuterium content of 96.2% d_1 (as determined by mass spectrometry): IR (neat) 2582 (C—D), 1977 cm^{-1} (C=C).

Vinyl triflate 5D was prepared from triflate **6** by following the same procedure as described for the preparation of triflate **3D**. It was obtained (200 mg; 60.3%) as a colorless oil with a deuterium content of 91.6% d_1 (as determined by mass spectrometry): IR (neat) 2585 (C—D), 1980 cm^{-1} (C=C).

Kinetic Studies. Solvents were prepared by weight from conductivity water (Millipore Systems) and appropriate organic solvents. Conductivity measurements were performed in sealed, paired cells by using a Hewlett-Packard Model 4274A LCR bridge, interfaced with a Hewlett-Packard Model 3497A multiplexer and a Hewlett-Packard Model 9826 BASIC microcomputer. From 1 to 10 μL (in-cell concentration was ca. 2×10^{-4} M) of a pentane solution of the triflate was utilized in the appropriate solvent buffered with 2,6-di*tert*-butylpyridine.

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Registry No. (**3H**), 84836-44-2; (**3D**), 98482-61-2; (**5H**), 79140-87-7; (**5D**), 98482-62-3; D_2, 7782-39-0.

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Facile Synthesis of the Four 3-Aminocyclopentane-1,2-diol Stereoisomers

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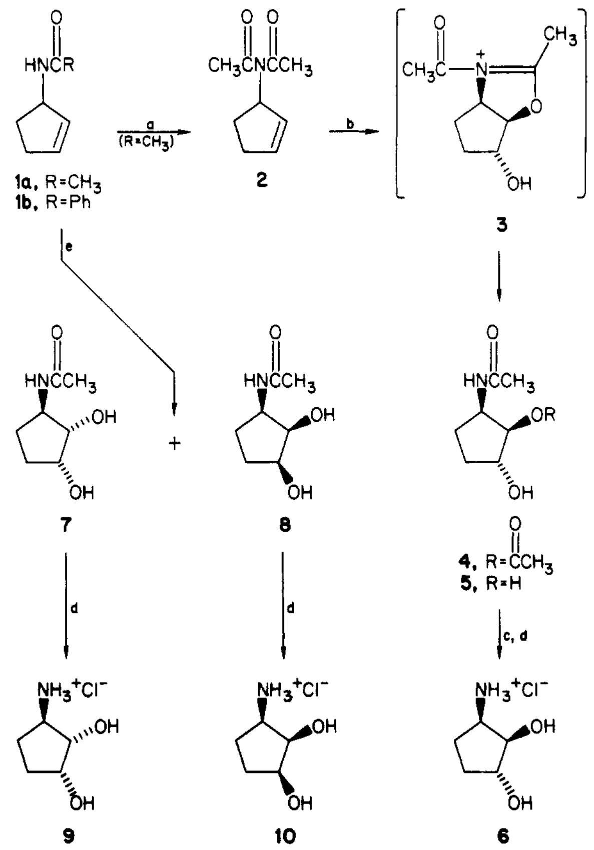
The 3-amino 1,2-diol functionality in five- and six-membered ring compounds occurs in many biologically active natural products, hence convenient synthetic routes to these compounds are desirable. For instance, the 3-amino 1,2-diol cyclopentyl function is not only present in both the parent[1] and reduced forms of nucleoside Q[2] but also has been used in the synthesis of nucleosides aristeromycin and neplanocin A.[3] Other examples of the occurrence of 3-amino 1,2-diol carbocyclic functionality are the aminocylitol antibiotics[4] such as 2-deoxyfortamine[5] and fortimicin aglycon[6] as well as the amino sugar antibiotics halacosamine[7] and garosaminide.[8]

Scheme I[a]



[a] (a) CH_3COCl, poly(4-vinylpyridine); (b) CF_3CO_3H; (c) K_2CO_3, MeOH; (d) $H_3O^+Cl^-$; (e) OsO_4, *N*-methylmorpholine *N*-oxide.

Since none of the diastereomers of 3-aminocyclopentane-1,2-diol have been previously reported, we have developed convenient synthetic routes to all four isomers.

The synthesis of the first stereoisomer, (1α,2β,3β)-3-aminocyclopentane 1,2-diol (**6**) (Scheme I), was approached via a novel intramolecular rearrangement. Conventional routes for the synthesis of **6**, including the hydrolysis of the epoxide **12**,[9] would require forcing conditions in polar solvents making the isolation and purification of **6** difficult.[10]

A synthesis in which the nitrogen on 3-acetamidocyclopentene (**1a**) controls the regio- and stereochemistry of the trans diol to be formed was envisioned as a con-

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