6A,6X-Dideoxy-6A-azido-6X-[(mesitylsulfonyl)oxy]-β-cyclodextrin (1–3). To a solution of 6-deoxy-6-azido-β-cyclodextrin[6] (250 mg) in dry pyridine (2 mL) was added mesitylenesulfonyl chloride (210 mg). The solution was stirred at room temperature for 9 h. The progress of reaction was monitored by TLC. The R_f value of the products (1–3) on TLC was 0.49. The amount of the sulfonyl chloride was dependent on the dryness of the reagents. After water (0.5 mL) was added to the solution to stop the progress of reaction, the mixture was concentrated in vacuo. The residue was dissolved in 20% aqueous EtOH (8 mL), filtered to remove the insoluble material, and chromatographed through a reversed-phase column (Lobar column LiChroprep RP18 Size B). After elution of water (500 mL), a gradient elution of water (300 mL)–30% aqueous MeOH (300 mL) followed by a gradient elution of 30% aqueous MeOH (800 mL)–80% aqueous MeOH (800 mL) was applied. Each fraction was monitored by UV absorption at 230 ann 270 nm and by TLC. The fractions of recovered starting material, **1**, **2**, or **3** were collected and concentrated in vacuo. The residue was dissolved in a small amount of water and lyophilized: the recovered starting material, 43.1 mg (28.7%); **1**, 19.4 mg (11.2%); **2**, 16.9% (9.7%); **3**, 14.9 mg (8.6%). The ^1H NMR spectra (Me_2SO-d_6) of **1–3** are very similar to each other: δ 2.29 (s, 3 H, CH_3), 2.54 (s, 6 H, 2 CH_3), 4.2–4.6 (5 H, OH), 4.65–5.00 (7 H, C_1H of cyclodextrin), 5.5–6.6 (14 H, OH), 7.10 (s, 2 H). The IR spectra (KBr) of **1–3** were also very similar to each other: 2100 (N_3), 1190, 1173, 760, 648 (sulfonate) cm^{-1}. FABMS: m/z 1142 (M + H), 1364 (M + Na).

Authentic 6A,6X-Dideoxy-6A,6X-diazido-β-cyclodextrin (4–6). A mixture of 6A,6B-dideoxy-6A,6B-bis(tosyloxy)-β-cyclodextrin[4] (30 mg) and sodium azide (40 mg) in dry DMF (0.7 mL) was stirred at 70 °C for 3 h. After evaporation of DMF in vacuo, the residue was dissolved in water (1 mL) and was applied on a reversed-phase column (Lobar column LiChroprep RP8 Size A). After elution of 10% aqueous EtOH (100 mL), a gradient elution of 10% aqueous EtOH (200 mL)–40% aqueous EtOH (200 mL) was used for the development. The fraction of the diazido-β-cyclodextrin was easily detected by monitoring the UV absorption at 210 nm. The fractions of the diazido-β-cyclodextrin were collected and concentrated in vacuo to give a pasty solid, which was dissolved in water and lyophilized to give **6**, 18 mg (73%). By the similar procedures, the 6A,6C- (**5**) (9.7 mg, 40%) and 6A,6D- (**4**) (14.3 mg, 48%) diazido isomers were prepared from the corresponding authentic ditosylates. The ^1H NMR spectra (D_2O) of **4–6** were very similar to each other: δ 5.0 (7 H, C_1H), 3.2–4.1 (other protons). The IR spectra (KBr) spectra of **4–6** were also very similar to each other: 2100 cm^{-1}. FABMS: m/z 1185 (M + H), 1207 (M + Na).

Conversion of 6A,6X-Dideoxy-6A-azido-6X-[(mesitylsulfonyl)oxy]-β-cyclodextrin to 6A,6X-Dideoxy-6A,6X-diazido-β-cyclodextrin. A mixture of 6A,6X-dideoxy-6A-azido-6X-[(mesitylsulfonyl)oxy]-β-cyclodextrin (**1**, **2**, or **3**) (15 mg) and sodium azide (11 mg) in dry DMF (0.5 mL) was stirred at 60 °C for 6 h. The progress of reaction was monitored by TLC. Only one product was detected by TLC (R_f 0.36). After evaporation of DMF in vacuo, the residue was dissolved in water (5 mL) and was adsorbed into a short reversed-phase column (SEP-PAK C_{18} cartridge, Waters Ltd.). After washing it with water (20 mL), 5% (10 mL), 10% (10 mL), 15% (10 mL), and then 20% (10 mL) aqueous EtOH solutions were stepwise applied. Concentration in vacuo and lyophilization of the 10% and 15% EtOH fractions gave 11 mg of 6A,6X-dideoxy-6A,6X-diazido-6β-cyclodextrin (**4**, **5**, or **6**). This product showed the correct molecular weight in the FABMS spectrum and demonstrated the same IR spectrum, the same R_f value on TLC, and the same retention time on HPLC as those of the corresponding authentic diazido-β-cyclodextrin **4**, **5**, or **6**.

Acknowledgment. We are indebted to Japan Maise Products Co. Ltd. for the generous gift of β-cyclodextrin.

Registry No. 6A,6D-**1**, 98126-94-4; 6A,6E-**1**, 98126-95-5; 6A,6C-**2**, 98169-86-9; 6A,6F-**2**, 98126-96-6; 6A,6B-**3**, 98126-97-7; 6A,6G-**3**, 98126-98-8; **4**, 98126-99-9; **4** (6A,6D-ditosylate), 95475-65-3; **5**, 98169-67-6; **5** (6A,6C-ditosylate), 95509-72-1; **6**, 80781-22-2; **6** (6A,6B-ditosylate), 95475-64-2; 6-deoxy-6-azido-β-cyclodextrin, 98169-85-8; mesitylenesulfonyl chloride, 773-64-8.

Crystal and Molecular Structure of *anti*-Sesquinorbornene[1]

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Since the recent preparation of the *syn*- and *anti*-sesquinorbornenes, **1**[3] and **2**,[4] respectively, several studies on their molecular structure and features associated with their molecular structure have been reported.[5-15] Theoretical calculations on the parent compound **1**[9-15] and X-ray structure analysis of several derivatives of *syn*-sesquinorbornene[7-9] and *syn*-oxasesquinorbornene[16] show that the syn isomer prefers a nonplanar, endo-bent arrangement around the double bond with the deviation from planarity being 12–22°. This conformation preference has been rationalized by diminished hyperconjugative destabilization by bending[13,14] and/or relief of unfavorable torsional interactions by bending.[15]

The molecular structure of *anti*-sesquinorbornene (**2**) has been a matter of dispute. Molecular mechanics calculations indicate a preference for a conformation with a bent double bond,[10-12] although Houk et al.[15] have shown that this preference disappears by eliminating torsional contributions. X-ray structure analysis has been reported

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(1) Systematic name: Tetracyclo[6.2.1.$1^{3,6}$.$0^{2,7}$]dodec-2(7)-ene. Previously named: 1,2,3,4,5,6,7,8-Octahydro-1,4:5,8-dimethanonaphthalene.

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(3) (a) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186. (b) Paquette, L. A.; Carr, R. V. C. *J. Am. Chem. Soc.* **1980**, *102*, 7553.

(4) Bartlett, P. A.; Blankency, A. J.; Kimura, M.; Watson, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 1383.

(5) Watson, W. H. "Stereochemistry and Reactivity of Systems Containing π Electrons"; Verlag Chemie International: Deerfield Beach, FL, 1983.

(6) (a) Bartlett, P. D.; Roof, A. A. M.; Winter, W. J. *J. Am. Chem. Soc.* **1981**, *103*, 6520. (b) Paquette, L. A.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *J. Org. Chem.* **1983**, *48*, 1250. (c) Paquette, L. A.; Charumilind, P.; Kravetz, T. M.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1983**, *105*, 3126. (d) Paquette, L. A.; Schaefer, A. G.; Blount, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3642. (e) Bartlett, P. D.; Roof, A. A. M.; Subramanyam, R.; Winter, W. J. *J. Org. Chem.* **1984**, *49*, 1875. (f) Paquette, L. A.; Hsu, L.-Y.; Gallucci, J. C.; Korp, J. D.; Bernal, I.; Kravetz, T. M.; Hathaway, S. J. *J. Am. Chem. Soc.* **1984**, *106*, 5743. (g) Kashyap, R. P.; Watson, W. H.; Wu, C.; Bartlett, P. D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 1851.

(7) Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022.

(8) (a) Paquette, L. A.; Hayes, P. C.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Blount, J. F. *J. Am. Chem. Soc.* **1983**, *105*, 3148. (b) Paquette, L. A.; Charumilind, P.; Böhm, M. C.; Gleiter, R.; Bass, L. S.; Clardy, J. *J. Am. Chem. Soc.* **1983**, *105*, 3136.

(9) Ermer, O.; Bödecker, C.-D. *Helv. Chim. Acta* **1983**, *66*, 943.

(10) Jørgensen, F. S. *Tetrahedron Lett.* **1983**, *24*, 5289.

(11) Ermer, O. "Aspekte von Kraftfeldrechnungen"; Wolfgang Baur Verlag: München, 1981.

(12) Johnson, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 1135.

(13) Gleiter, R.; Spanget-Larsen, J. *Tetrahedron Lett.* **1982**, *23*, 927.

(14) Spanget-Larsen, J.; Gleiter, R. *Tetrahedron* **1983**, *39*, 3345 and references therein.

(15) Houk, K. N.; Rondan, N. G.; Brown, F. K.; Jorgensen, W. L.; Madura, J. D.; Spellmeyer, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 5980 and references therein.

(16) (a) Hagenbuch, J. D.; Vogel, P.; Pinkerton, A. A.; Schwarzenbach, D. *Helv. Chim. Acta* **1981**, *64*, 1818. (b) Watson, W. H.; Galloy, J.; Grossier, D. A.; Bartlett, P. D.; Combs, F. L. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 1050.

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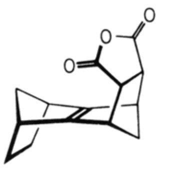
2



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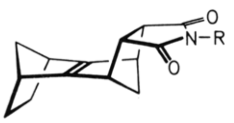

4

R = $C_6H_4NO_2$

for several derivatives of *anti*-sesquinorbornene;[7-9] for example, the anti-endo derivative **3** contains a planar double bond[7] whereas the anti-exo derivative **4** is considerably puckered with the double bond deviating from planarity by 13.2 (3)°.[9] Furthermore, a recent photoelectron spectroscopic determination of the π_{CC} ionization energies for the two sesquinorbornenes (**1**, 8.12 eV; **2**, 7.90 eV)[17] supports the notion that the molecular structures are fundamentally different, i.e., implicitly suggesting the anti isomer **2** to be planar.

To determine whether the double bond moiety in the parent compound *anti*-sesquinorbornene (**2**) actually is planar or bent, a crystal structure determination has been performed simultaneously by two groups and the results are reported in this joint paper.

Results and Discussion

The crystals of *anti*-sesquinorbornene (**2**) are monoclinic, space group $P2_1/n$. The unit cell contains two molecules. Due to the crystallographic symmetry the molecule must possess a center of symmetry. This is consistent with either a planar or a twisted arrangement of the double bond. The positional parameters are listed in Table I, and a perspective drawing of the molecule is shown in Figure 1.

The most interesting feature of the molecular structure is the planar arrangement around the double bond, the torsional angle C1–C6–C6′–C4 being 0.2 (1)°. This confirms the preference for planarity of the double bond in the parent anti isomer, and it is consistent with previously reported X-ray structure investigations of several *anti*-sesquinorbornene derivatives.[7,8] The X-ray diffraction data of **2** were collected at low temperature (105 K as well as 243 K). The parameters derived from the 105 K study are of higher accuracy with standard deviations typically being 3 times lower, and the following discussion is based mainly on this study. Inspection of the thermal parameters of the heavy atoms (cf. Table II supplementary material) indicates that the double bond atoms (C6 and C6′) have a relatively high amplitude for motion perpendicular to the plane of the double bond or a small displacement of the C6 and C6′ positions out of the plane (cf. Figure 2, supplementary material). Both cases support the notion that little energy is required to perform a puckering of the molecule. The energy increase associated with a 1° bending from planarity has previously been calculated to be 13 cal/mol for *anti*-sesquinorbornene (**2**).[15] All distances in the 243 K study are within 3σ of those in the 105 K study except for those involving the sp^2 carbon atoms. This is consistent with increased movement of these atoms as the temperature increases.

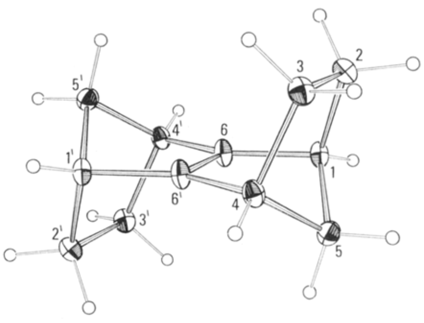

Figure 1. ORTEP[27] drawing of the molecular structure of *anti*-sesquinorbornene (**2**). Thermal ellipsoids are drawn at the 50% probability level.

Table I. Final Atomic Parameters for *anti*-Sesquinorbornene (2)[a]

atom	x	y	z	B_{eq}, Å^2
C1	0.9616 (1)	0.24642 (8)	−0.01282 (6)	0.950 (9)
C2	0.7265 (1)	0.25714 (9)	0.03072 (7)	1.101 (9)
C3	0.7502 (1)	0.13533 (9)	0.16159 (7)	1.102 (9)
C4	0.9959 (1)	0.06833 (8)	0.17900 (6)	0.928 (9)
C5	1.1065 (1)	0.24110 (9)	0.13174 (7)	1.092 (9)
C6	0.9897 (1)	0.05224 (9)	−0.05642 (6)	0.993 (9)
H11	0.994 (2)	0.344 (2)	−0.074 (1)	1.9 (2)
H21	0.606 (2)	0.213 (2)	−0.043 (1)	2.0 (2)
H22	0.690 (2)	0.385 (2)	0.051 (1)	2.3 (2)
H31	0.645 (2)	0.029 (1)	0.150 (1)	1.3 (2)
H32	0.721 (2)	0.205 (2)	0.243 (1)	1.5 (2)
H41	1.051 (2)	0.021 (1)	0.270 (1)	1.3 (2)
H51	1.082 (2)	0.348 (27)	0.186 (1)	2.1 (2)
H52	1.269 (2)	0.233 (2)	0.128 (1)	1.8 (2)

[a] Estimated standard deviations are in paratheses. Hydrogen atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $B(\text{Å}^2) = (4/3)[a^2\beta(1,1)b^2\beta(2,2)c^2\beta(3,3)ac\cos\beta\,\beta(1,3)]$.

Comparison of the parent molecule **2** with the endo-anhydride **3** and exo-imide **4** derivatives reveals that the introduction of the endo bridge to give **3** does not affect the puckering of the molecule in contrast to introduction of the exo bridge to give **4**. Simple steric considerations cannot explain satisfactorily why the exo-imide **4** is nonplanar in contrast to the parent compound **2** and the endo-anhydride **3**. From a study of the structures of different substituted endo derivatives of *anti*-sesquinorbornene, Paquette et al.[8] have shown the maximum deviation from planarity to be 2.0°, suggesting that intramolecular nonbonding steric factors are unimportant. The increase in molecular size from **2** to **4** probably affects the crystal packing, and by taking advantage of the low out of plane bending force constant the exo imide avoids unfavorable intermolecular nonbonding interactions.

The rigidity of the norbornene skeleton is reflected in the structure of *anti*-sesquinorbornene (**2**), which shows bond lengths, bond angles, and angles between planes similar to values found for simple norbornene derivatives.[4,18] The C6–C6′ bond length, 1.343 Å, is a normal value. The major deformations are observed around the double bond with the internal (C1–C6–C6′ and C4′–C6–C6′) and external (C1–C6–C4′) bond angles being 108.09 (5)°, 108.13 (5)°, and 143.78 (5)°, respectively. There is a close relationship between the puckering of the molecule

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(17) Brown, R. S.; Buschek, J. M.; Kopecky, K. R.; Miller, A. J. *J. Org. Chem.* **1983**, *48*, 3692.

(18) (a) Bartlett, P. D.; Combs, G. L., Jr.; Le, A.-X. T.; Watson, W. H.; Galloy, J.; Kimura, M. *J. Am. Chem. Soc.* **1982**, *104*, 3131. (b) Filippini, G.; Gramacciolo, C. M.; Rovere, C.; Simonetta, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 2869. (c) Destro, R.; Filippino, G.; Gramaccioli, C. M.; Simonetta, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1969**, *B25*, 2465.

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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(19) Burkert, U.; Allinger, N. L. "Molecular Mechanics"; American Chemical Society: Washington, DC, 1982; ACS Monogr. No. 177.

(20) Kopecky, K. R.; Miller, A. J. *Can. J. Chem.* **1984**, *62*, 1840.

(21) Overbeck, A. R.; Schenk, H. In "Computing in Crystallography"; Schenk, H., Olthof, R., van Koningsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, 1978; p 108.

(22) Structure Determination Package, ENRAF-NONIUS, Delft, Holland.

(23) Cromer, D. T.; Mann, J. B. *Acta Crystallogr. Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 321.

(24) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(25) Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data"; University of York, England, and University of Louvain, Belgium, 1978.

(26) Stewart, J. M.; Machin, P. A.; Dickinson, C. W.; Ammon, H. L.; Heck, H.; Flack, H. Technical Report TR-446; Computer Science Center: University of Maryland, College Park, 1976.

(27) Johnson, C. K. Report ORNL-3794, 2nd revision; Oak Ridge National Laboratory: Oak Ridge, TN, 1970.

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

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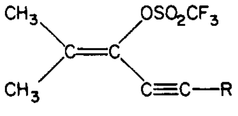
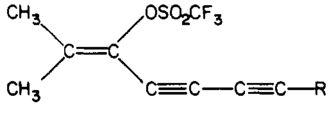
There are few cases where the remote secondary deuterium effect involving an alkynyl group has been examined. The isotope effect upon deuterium substitution in the 1-position of 3-chloro-3-methyl-1-butyne was reported[1] to be $k_H/k_D = 1.00 \pm 0.04$. To our knowledge, the only other examples of a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