Carbon Cluster Compounds. Generation and Reorganization of the Homobullvalenyl Cation, an 11-Fold Degenerate Species[1]

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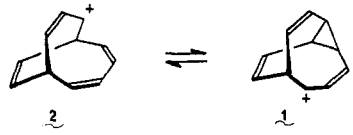
Abstract: Treatment of 4-bromo-4-trifluoroacetoxytetracyclo[4.3.2.$0^{2,9}$.$0^{3,5}$]undeca-7,10-diene (**3**) with sodium borohydride gave *endo*-4-hydroxytetracyclo[4.3.2.$0^{2,9}$.$0^{3,5}$]undeca-7,10-diene (**5**). Acetolysis of the corresponding triflate (**9**) proceeded at a rate virtually identical with those of the dihydro and tetrahydro derivatives **10** and **11**. Solvolysis of the specifically deuterated triflate **9**-*d* gave the alcohols **12** and **13** which were shown to have a statistical distribution of deuterium among the 11 skeletal carbons. This scrambling process has been interpreted in terms of multiple rearrangement paths of the intermediate homobullvalenyl and bicyclo[4.3.2]undecatetraenyl cations **1** and **2**.

The chemistry of carbocyclic cluster ions of the $[CH]_n$ type has attracted sustained attention owing to the unique opportunities these systems present for unusual modes of p-orbital confrontation and the novelty of the reactions often resulting from these interactions.[2] The homobullvalenyl cation (**1**) and its valence tautomer, the bicyclo[4.3.2]undecatetraenyl cation (**2**), are particularly interesting in this regard since



knowledge of their behavior may provide evidence as to the extent and nature of any "homoaromatic"[3] or "bicycloaromatic"[4] effects in these ions.

Multiple, degenerate rearrangements of **1** and **2** can be envisaged which, in analogy to the isoelectronic hydrocarbon bullvalene, can ultimately result in complete positional scrambling. We describe here a synthetic approach to **1** and **2** which has led to the conclusion that the homobullvalenyl cation (**1**) is indeed fully degenerate but that there is no evidence for extraordinary stabilization or destabilization in either **1** or **2**.[5]

Results and Discussion

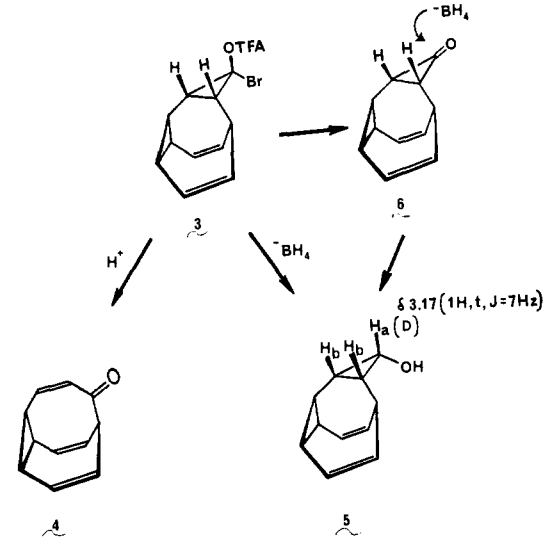
Synthesis. The ready availability in our laboratories of the α-bromotrifluoroacetate **3**[6] has provided both a convenient entry into the family of valence tautomeric $C_{11}H_{10}O$ ketones[7,8] and a route to the parent $[CH]_{11}$ system.[5] The reduction of **3** with sodium borohydride afforded a 77% yield of the corresponding cyclopropanol **5** (Scheme I).

The spectral properties of **5** indicated that it was a fluxional, bridged homotropilidene.[9] A new triplet in the ^{1}H NMR spectrum (δ 3.17) of **5** could be assigned to the hydroxymethine proton (H_a). The magnitude of the coupling constant (J_{ab} = 7 Hz) clearly indicated cis vicinal proton coupling and, accordingly, the endo stereochemistry.[10] Further, spin decoupling at the position of H_b (δ 0.88) resulted in the collapse of the H_a resonance to a singlet and treatment of **3** with sodium borodeuteride produced **5**-*d* (>98% D) lacking the resonance at δ 3.17.

Conceptually, the sole formation of the endo cyclopropanol can best be explained by the intermediacy of a cyclopropanone (**6**) and subsequent hydride delivery from the least hindered side.[11]

The relatively hindered cyclopropanol **5** turned out to be difficult to functionalize under normal conditions. Thus, treatment of **5** with 2,4-dinitrobenzoyl chloride afforded little

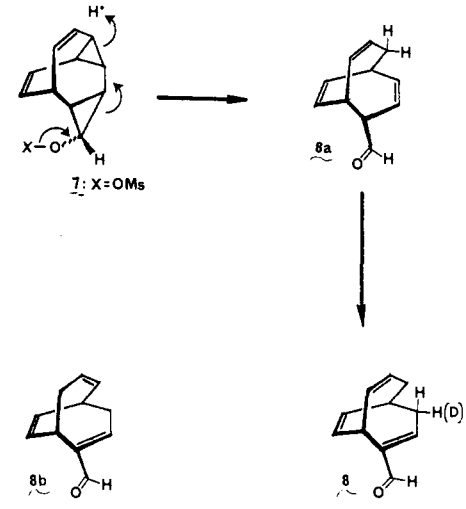
Scheme I



ester. Treatment of **5** with methanesulfonyl chloride produced a 73% yield of the corresponding mesylate (**7**). **7** was a stable, crystalline compound which could be characterized by routine analytical procedures.

Solvolysis of **7** in buffered acetic acid afforded an aldehyde **8** in over 80% yield. **8** was also produced directly from **5** upon standing or treatment with $AlCl_3$ in ether (Scheme II).

Scheme II



The structure of **8** was discerned from its ^{1}H NMR spectrum, particularly the *singlet* aldehyde resonance (δ 9.27) and a triplet for the proton β to the carbonyl (δ 6.75). This latter resonance appeared as a *doublet* when the conversion of **7** to **8** was run in acetic-d_3 acid-d_1. Thus, the $\beta,\gamma \rightarrow \alpha,\beta$ tautomerism (**8a** → **8**) takes a proton from the solvent as expected. The assigned position of the remaining double bond (**8** or **8b**), though less secure, was made by noting the marked dissimilarity in the chemical shifts of the two bridgehead protons (δ 2.95 and 3.6). The apparent preference for O–S bond cleavage observed here seems to indicate a resistance to carbonium ion formation.

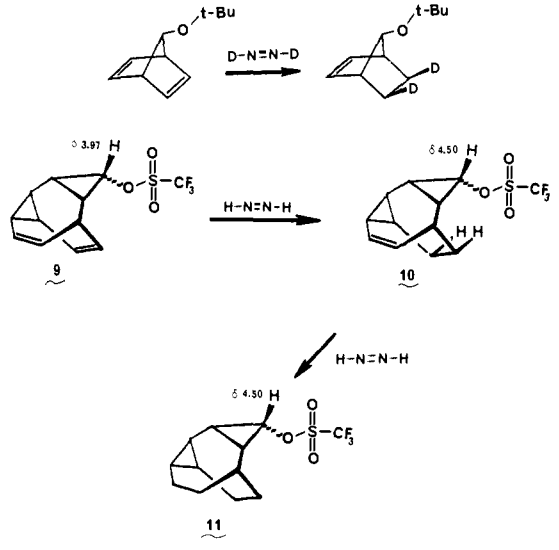
Ultimately, the triflate **9** was synthesized (99% yield) by the treatment of **5** with trifluoromethanesulfonyl anhydride. This triflate (**9**) was moderately stable in air and, surprisingly, could be purified by preparative thin layer chromatography. Subsequent solvolyses of **9** were performed immediately after purification. The ^{1}H NMR spectrum of **9** was similar to those of **5** and **7** except that the oxymethine proton and its characteristic coupling constant were obscured by the four-proton multiplet (δ 3.97) of the fluxional homotropylidene moiety. Inasmuch as a definitive stereochemical assignment was crucial for proper analysis of any eventual solvolysis data, the variable temperature ^{1}H NMR spectrum of **9** in the region of δ 3.97 was determined (Figure 1). As anticipated for the assigned structure, a portion of the complex five-proton multiplet broadened gradually with decreasing temperature until at −70 °C a one-proton triplet (δ 3.97, J = 7 Hz) was clearly evident. Accordingly, the endo stereochemistry had been preserved in the conversion of **5** to **9.**

As potential solvolytic comparators to the behavior of **9** the corresponding dihydro and tetrahydro derivatives **10** and **11** were prepared. Thus, treatment of **9** with 5 equiv of potassium diazodicarboxylate[12,13] afforded **10** (54%) and **11** (11%). The spectral data of **10** and **11** clearly indicated two cyclopropanes and the intact endo-triflate group. Similarly, treatment of bullvalene with diimide has been found to lead to sequential double bond reduction without disturbing the cyclopropane.[14]

Surprisingly, only *one* monoolefin (**10**) was obtained in this reaction. Diimide reductions have been shown to be generally sensitive to steric approach control.[13] A remarkable exception is the hydrogenation of 7-substituted norbornadienes by diimide. Thus, the reduction of 7-*tert*-butoxynorbornadiene proceeds by syn-exo addition, apparently revealing a directive effect of the neighboring oxygen.[15]

Molecular models indicate that a similar geometrical relationship exists between the oxygen and π bond for 7-*tert*-butoxynorbornadiene (2.6 Å) and **9** (2.2 Å). Significantly, conversion of **9** to its dihydro derivative (**10**) resulted in a 0.55 ppm *downfield* shift in the ^{1}H NMR resonance due to the oxymethine proton while no further change was observed upon reduction of **10** to **11.** We have ascribed this shift to changes in the steric and electronic environment of the triflate group, supporting a regioselective reduction of the syn double bond in **9** to yield exclusively **10** (Scheme III). It should be noted that the double bond that remains in **10** is advantageously positioned for possible bishomoconjugative interactions upon solvolytic cyclopropane ring opening.

Scheme III



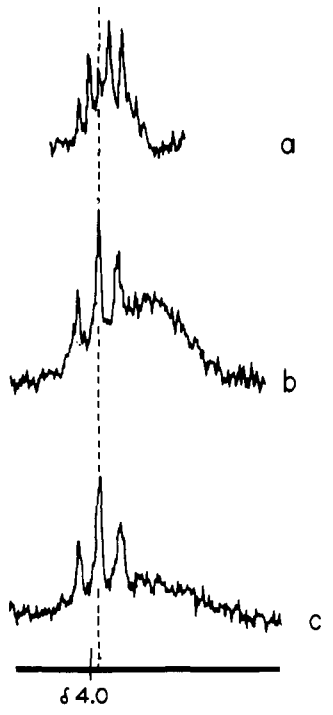
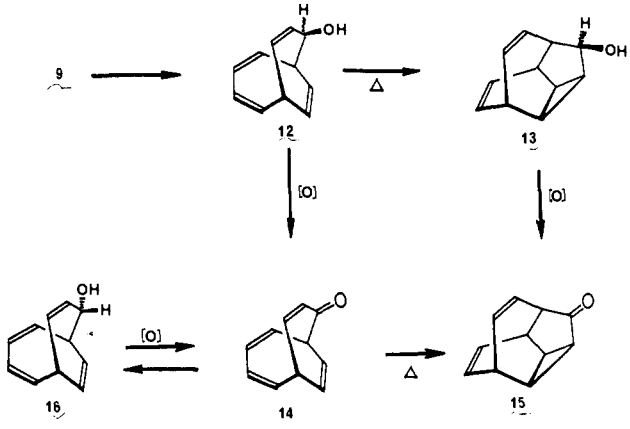


Figure 1. Variable temperature ^{1}H NMR spectrum of **9**: (a) at 25 °C; (b) at −48 °C; (c) at −70 °C.

Solvolysis. Solvolysis of **9** in 40% aqueous acetone for 3 h at 90 °C produced a mixture of two alcohols, **12** and **13,** which upon Sarett oxidation provided two known ketones, **14**[8d] and **15**[7a] (17:83), in a 65% isolated yield (Scheme IV).

Scheme IV

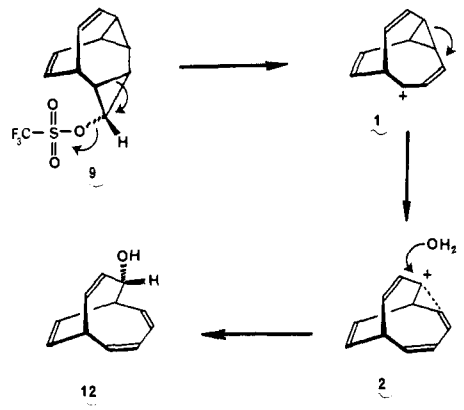


The initial solvolysis product (**12**) was established to be an epimer of the known alcohol **16**[8d] by observing their mutual conversion to **14** upon mild oxidation.

The origin of **12** is readily explained by initial solvolytic ring opening of **9** to give the homobullvalenyl cation (**1**) and subsequent cyclopropylcarbinyl → homoallyl reorganization to produce the bicyclo[4.3.2]undecatetraenyl cation (**2**). Capture

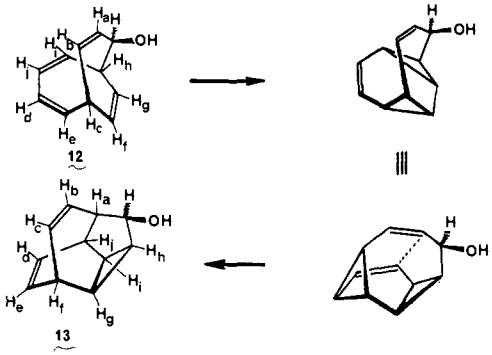
of **2** by water stereoselectively on the exo side of the allyl cation would then give **12** as observed. This stereochemical preference, the same that is observed upon hydridic reduction of the corresponding ketone (**14**),[8c] is difficult to assess but lies in the expected direction if the allylic cation moiety in **9** is stabilized by electronic delocalization of the diene π bonds (Scheme V).

Scheme V



The thermal conversions **12** → **13** and **14** → **15** have been shown to result from an intramolecular [4 + 2] cycloaddition followed by a Cope rearrangement of the resultant cis divinylcyclopropane (Scheme VI).[7b,8c] Thus, every hydrogen in **12** can be related to a unique hydrogen in **15**.

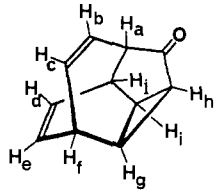
Scheme VI



Deuterium Scrambling. As a test of Scheme V and a probe for possible degenerate behavior of **1** or **2**, **9**-*d* was solvolyzed in aqueous acetone, and pure **12**-*d* was isolated from the reaction mixture. The ^{1}H NMR spectrum of **12**-*d* showed five resonances indistinguishable from integral values (see Experimental Section). The product alcohols (**12**-*d* and **13**-*d*) were oxidized with CrO_3–pyridine to **14**-*d* and **15**-*d*. The mass spectrum of **15**-*d* indicated loss of 0.11 deuterium atoms compared to **9**-*d*. Further, the ^{1}H NMR spectrum of **15**-*d* (Figure 2) indicated no significant reduction of any of the proton resonances (Table I). Accordingly, the conversion of **9**-*d* to **15**-*d* did not proceed in as simple a manner as depicted in Scheme V and Scheme VI; rather, the solvolysis of **9**-*d* must have been accompanied by extensive skeletal reorganization.

The extent of this scrambling was elucidated by comparing observed and calculated ^{1}H NMR spectra of **15** and **15**-*d*. The observed spectra were sufficiently well resolved that distinct deuterium satellites could be observed in the spectrum of **15**-*d* (Figure 2) where **15** had clear valleys (<3%). The ratio of the intensities of the deuterium satellite peaks to those of the parent resonance were both easily calculable for various possible rearrangement schemes and measurable from the spectrum of **15**-*d* (see Experimental Section). Table II lists calculated ^{1}H

Table I. Intensities of Protons in **15**-*d*



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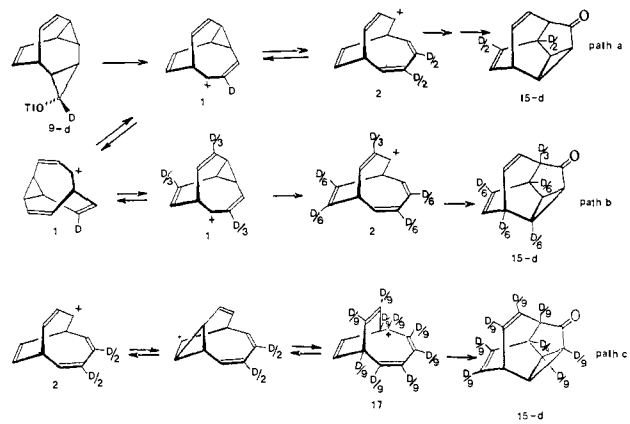
Proton	Chemical shifts, δ, in $CDCl_3$	Normalized area[a]	Calcd proton for D/11
a	2.85	0.93	0.91
b	5.42	0.97	0.91
c	6.58	0.93	0.91
d	5.91	0.94	0.91
e	6.66	0.87	0.91
f	3.19	0.93	0.91
g	1.97	1.78	0.91
h	2.04		0.91
i	2.50	0.95	0.91
j	3.51	0.91	0.91

[a] Values adjusted to reflect total D content of **15**-*d*. Peak intensities were determined by digital integration of Figure 2. Results were in agreement with manual techniques.

NMR deuterium satellite intensities (*D*) for three processes which appear most likely to contribute to the degeneracy of **1** or **2** (Scheme VII). Figure 3 compares the observed resonances

Scheme VII



for H_c and H_e in **15**-*d* with computer-simulated spectra corresponding to 11-fold (*D* = 0.24) and 9-fold (*D* = 0.12) scrambling.

Cyclopropylcarbinyl–homoallyl interconversions of **1** and **2** (path a), a circumambulation of the butadiene moiety in **2** about the remainder of the molecule, does not lead to any further distribution of the deuterium label by itself but when coupled with the degenerate Cope rearrangement of the homotropylidene complete degeneracy can be ultimately achieved.

Path b depicts successive cyclopropylcarbinyl–cyclopropylcarbinyl rearrangements which ultimately result in a threefold scrambling of the label in **1a** and a five-carbon distribution in **15**. The sole intervention of this mechanism as an explanation of the observed results is clearly eliminated by the lack of significant deuterium label at H_a (<0.08) and the similarity in the observed deuterium satellite intensities for H_b and H_c. Path b demands D/3 at H_a and deuterium satellite intensities of 0.41 and 0.17 for H_b and H_c, respectively.

The simultaneous operation of paths a *and* b will distribute some deuterium label to all positions after only two cycles and eventually a statistical distribution will be observed.

Table II. Relative ^{1}H NMR Deuterium Satellite Intensities[a] for **15-*d*** Derived from Various Rearrangements

Protons	a	b	c	d	e	f	g	h	i	j
D (a)	0.26	0.41	0.17	0.20	0.41	0.20	0.20	0.17	0.41	0.51
D (b)	0	0	0.76	0	0.76	3.1	3.1	0.76	0.76	0
D (c)	0.27	0.27	0.12	0.27	0.12	0.24	0.24	0.14	0.33	0.59
D (obsd)	0.22	0.25	0.24	0.27	0.23	0.38			0.35	
D (statistical)	0.24	0.24	0.24	0.24	0.24	0.40	0.40	0.24	0.40	0.40

[a] Observed relative deuterium satellite intensities were determined by digital integration of Figure 2 from inflection to inflection (Digilab software). The results were consistent with manual techniques (see Experimental Section).

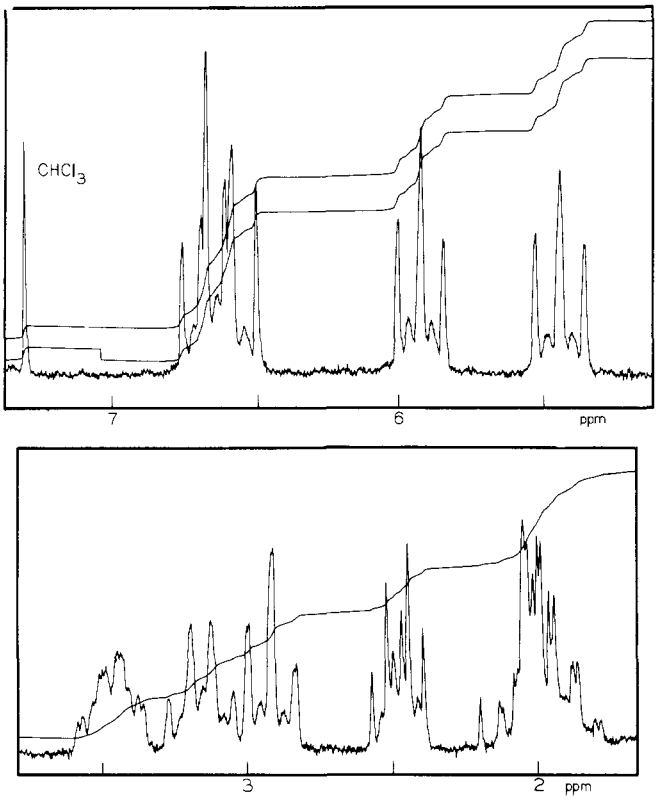


Figure 2. ^{1}H NMR spectrum of **15-*d*** determined in $CDCl_3$ at 100 MHz.

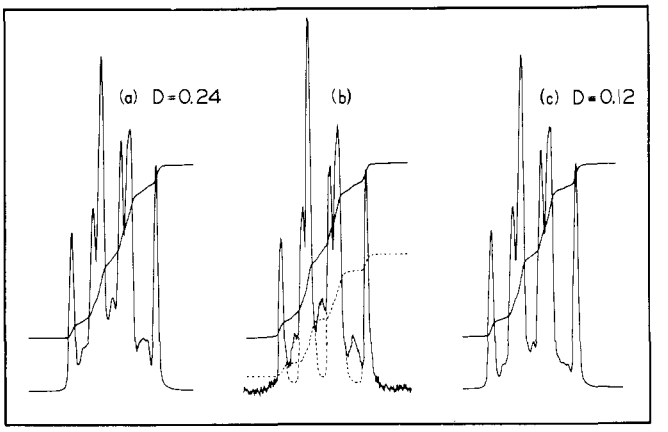


Figure 3. Calculated and observed ^{1}H NMR resonances for H_c and H_e (δ 6.58 and 6.66) in **15-*d***: (a) calculated spectrum expected for statistical scrambling (D = 0.24); (b) H_c and H_e as observed in **15-*d***, - - - - H_c and H_e as observed in **15**; (c) calculated spectrum for ninefold scrambling (D = 0.12, path c).

Homoallyl–cyclopropylcarbinyl interconversions involving the ethylidene bridge in **2** (path c) also appear to provide a mode of deuterium scrambling. This single process, which may be regarded as a circumambulation of the two-carbon bridge in **2** about the remaining nine-carbon ring, results in a ninefold positional scrambling in both **12** and **15** if the process is restricted to a single two-carbon migrating unit and complete 11-fold scrambling if the two ethylidene bridges in the intermediate **17** become equivalent by symmetry.[16]

The deuterium satellite intensity data clearly rule out the sole intervention of path a, path b or path c. Rather, the similarity between observed and calculated satellite intensities for D = 0.24 (Figure 3) are consistent only with complete randomization of the label to all 11 carbons by some combination of these mechanisms.[17] A degenerate Cope rearrangement in **1** would certainly be too slow to contribute significantly to the observed scrambling.[9] Likewise, models indicate that relatively extreme bond angle deformations are required to convert **2** to **17** (path c). This analysis leaves paths a and b as the most likely contributors. Thus, the rapid rearrangements which have precedent in simple cyclopropylcarbinyl ions[18] can serve here to afford an unprecedented degree of carbonium ion degeneracy.

Kinetics. Solvolysis rates of substituted cyclopropanol derivatives have been shown to increase as the substitution stabilizes the developing allylic cation.[18] Accordingly, the relative rates for **9, 10,** and **11** should provide an indication of the extent of any homoconjugate or longicyclic interactions upon development of an allylic cation in these molecules. In fact, **9, 10,** and **11** have been found to solvolyze in acetic acid at remarkably slow and nearly identical rates (Table III). The lack of any effect of the degree of saturation on the solvolysis rate supports the view that there is little if any homoaromatic or bicycloaromatic contribution to the transition state of ring opening. Rather, the sluggishness of these compounds can be attributed to bond angle deformations required to develop a planar allylic cation. Inspection of molecular models indicates that **9, 10,** and **11** should all resist the development of a planar allylic cation. Hence, concerted cyclopropyl ring opening upon solvolysis, which must approach a planar allylic cation, is restricted by developing *I* strain.

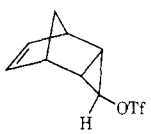
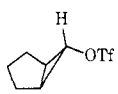
The acetolysis of *endo*-7-norcaranyl triflate (**18**) is ca. 10^2 faster than that of **9, 10,** and **11** at 100 °C indicating that this *I*-strain barrier is in the range of 3.0–3.6 kcal. In contrast, the *exo*-cyclopropyl triflates **19** and **20,** which probably have little ring-opening participation, solvolyze ca. 10^3 times *slower* than **9, 10,** and **11**.[20]

It is possible that the similarity of the rates is due to a fortuitous cancellation of opposing factors—favorable π-bond participation and inductive olefinic deceleration. Since this latter effect has been shown to amount to only a tenfold rate factor,[19] any opposing acceleration due to favorable delocalization must also be small.

Conclusion

It is clear from the results described above that the solvolysis of **9** has led cleanly and unequivocally to the **1** ⇄ **2** manifold. The solvolysis studies have demonstrated no unusual acceler-

Table III. Kinetic Parameters of Cyclopropyl Triflates

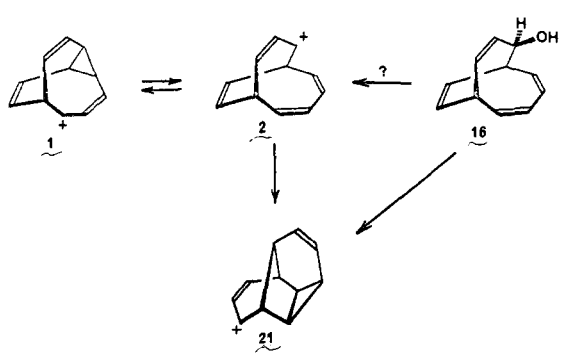
Compd	Temp, °C (±0.2 °C)	k, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
	100	$2.4 \pm 0.2 \times 10^{-4}$ [a]		
	70.4	$1.9 \pm 0.3 \times 10^{-4}$ [b]	29	+9.7
	74.1	$2.9 \pm 0.2 \times 10^{-4}$ [b]		
9	79.0	$3.1 \pm 0.5 \times 10^{-4}$ [b]		
	85.0	$6.7 \pm 0.5 \times 10^{-4}$ [b]		
	89.0	$1.6 \pm 0.1 \times 10^{-3}$ [b]		
	93.0	$2.7 \pm 0.4 \times 10^{-3}$ [b]		
10	100	$1.6 \pm 0.3 \times 10^{-4}$ [a]		
11	100	$1.5 \pm 0.3 \times 10^{-4}$ [a]		
18	100	1.3×10^{-2} [a,c]		
		3.28×10^{-2} [a,d]		
 **20**	100	5.31×10^{-7} [e]	32.7	−0.1
 **19**	100	1.5×10^{-7} [e]	32.3	−4.3

[a] Acetic acid buffered with 0.1 M sodium acetate. [b] 40% aqueous acetone buffered with 0.05 M 2,6-lutidine. [c] Private communication, P. G. Gassman. [d] T. M. Su, Ph.D. Thesis, Princeton University, 1970. [e] Cf. ref 20.

ation or deceleration as a function of the degree of unsaturation and we must conclude that any bishomoaromatic or bicycloaromatic effects are small or nonexistent in the development of this cation. The structure of the ion produced, whether **1** or **2** or some more highly delocalized hybrid, cannot be determined at this time. The fact that a covalent derivative of **2** is the sole initial product may be used to argue in favor of **2** as the local energy minimum. The exclusive formation of the anti alcohol **12** upon solvent capture of the carbonium ion is consistent with π-bond participation on the other face of the allyl bridge in **2**, a distortion in the direction of structure **1**.

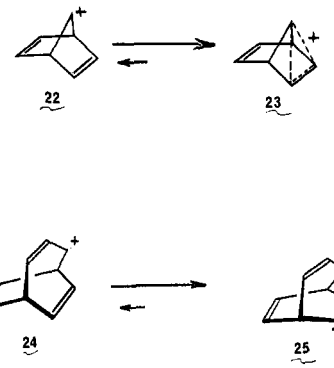
This distinction is a moot one, however, since, inasmuch as the observed scrambling is due to rapid cyclopropylcarbinyl ↔ homoallyl interconversions of **1** and **2**, the two structures cannot be more than 2–3 kcal apart in energy.

The successful approach to **1** and **2** from **9** contrasts with the rapid rearrangement of **16** to **21** in superacid observed by



Goldstein.[8b] Apparently **21** is thermodynamically more stable than **1** or **2** and **2**, if produced from **16**, rearranges rapidly and irreversibly under these conditions. This facile rearrangement is a further indication that **1** ⇄ **2** is not appreciably stabilized.

It is of interest to compare the behavior of the bicyclo[4.3.2]-undecatetraenyl cation manifold (**1** ⇄ **2**) described here to earlier results for the corresponding [2.2.1] and [3.2.2] systems, **22** ⇆ **23** and **24** ⇄ **25**, particularly with regard to the



conceptual and theoretical framework that has been advanced concerning these compounds.[3,4]

Solvolysis data indicate that while bishomoaromatic interactions in a developing 7-norbornadienyl cation are a major stabilizing influence the second double bond affords relatively little additional stabilization.[21] Low-temperature ^{1}H NMR data support this view. The [2.2.1] cation is found to be strongly distorted in the direction of **23**, an ethylidene-bridged bishomocyclopropenyl cation.[22] A sevenfold carbon scrambling process which has been presumed to involve the bridge-flip rearrangement **22** ⇄ **23** has an appreciable energy barrier (≥19.6 kcal/mol). Accordingly, either the predicted[4] bicycloaromatic stabilization of **22** is absent or overwhelmed by more significant factors such as angle strain.

The bicyclo[3.2.2] cation (**24**) is not formed solvolytically from its covalent derivatives; rather the barbaralyl cation (**25**) is formed synchronously with ionization.[23] While this observation can be used to support electronic *destabilization* of **24**, as predicted, the result is also in accord with *stabilization* of **25**. The difference in energy between **24** and **25** must be small and has been estimated to be ≤6 kcal/mol. The singlet ^{1}H NMR spectrum observed for **25** in superacid indicates that the **24** ⇆ **25** interconversion must be rapid under these conditions. Incomplete scrambling has been observed solvolytically, however.[23c,d]

The barrier to skeletal scrambling has been lowered further in the bicyclo[4.3.2] manifold (**1** ⇄ **2**) since complete degeneracy is observed during the solvolytic conversion of **9** to **12** under conditions which give only partial equilibration in **25**. Accordingly, the energy difference between **1** and **2** can only be ca. 2–3 kcal/mol.

The isolation of **14** by capture of **2** is in formal agreement with predictions that longicyclic effects which destabilize **24** should stabilize **2**.[4] Given the size of the energy differences involved (similar to the rotational barrier of ethane!) and the lack of any π-bond effects on the observed solvolysis rates, again no evidence for significant stabilizing influences has been found. Nevertheless, the homobullvalenyl cation manifold (**1** ⇄ **2**) has been shown to be the most highly degenerate carbon-framework compound observed to date.

Experimental Section

General. All melting points were taken on a capillary melting apparatus (Thomas-Hoover) and are uncorrected. Nuclear magnetic resonance spectra were recorded on either a Varian T-60 or JEOL PS-100 spectrometer. The JEOL PS-100 NMR spectrometer and Digilab software were used to obtain the FT ^{13}C NMR and FT ^{1}H NMR spectra. Infrared spectra were taken on either a Perkin-Elmer 457 or 237B spectrophotometer. Ultraviolet spectra were recorded on a Cary Model 14 spectrophotometer. All infrared spectra were taken in CCl_4 and all NMR spectra were taken in $CDCl_3$ (99.8%).

Mass spectra were run on either an Associated Electrical Industries MS-902 spectrometer or Associated Electrical Industries MS-30 double beam mass spectrometer with a Pye 104 gas chromatograph and AEI-DS-30 data system.

Analytical vapor phase chromatographic data were obtained with

a Varian Aerograph gas chromatograph Model 1200 equipped with a flame ionization detector. Preparative GLC was done on a Varian Aerograph 90-P gas chromatograph equipped with a thermal conductivity detector. Brinkmann thin layer plates precoated with silica gel or alumina (0.025 and 2 mm) and fluorescent indicator were used for analytical and preparative thin layer chromatography. Woelm silica gel or basic alumina (activity 1) were used for column chromatography.

4-Bromo-4-trifluoroacetoxytetracyclo[4.3.2.0^{2,4}.0^{8,9}]undeca-7,10-diene (3). To a solution of 0.5 g (1.65 mmol) of 4,4-dibromotetracyclo[4.3.2.0^{2,9}.0^{3,5}]undeca-7,10-diene[7c] in 7 mL of distilled and recrystallized benzene 1.09 g (4.93 mmol) of dry silver trifluoroacetate (Aldrich) was added all at once. The solution, which became momentarily homogeneous, was refluxed for 3 h under an inert atmosphere in the absence of light. The reaction mixture was decanted into 25 mL of water and extracted with 50 mL of ethyl ether. The organic extract was washed with water (4 × 100 mL), 5% sodium bicarbonate (2 × 50 mL), and saturated sodium chloride solution (3 × 100 mL) and dried over anhydrous sodium sulfate. Evaporation of the solvent gave 0.498 g (90%) of the α-bromocyclopropyl trifluoroacetate **3** and about 5% of the unreacted starting material. Subsequent transformations of **3** were carried out with this mixture.

IR (CCl_4) 3060, 2060, 1790, 1340, 1320, 1220, 1180, 1125 cm^{-1}; NMR ($CDCl_3$) δ 1.7 (2 H, triplet), 2.5 (2 H, multiplet), 3.9 (4 H, multiplet), 5.75 (2 H, triplet); mass spectrum (45 eV) *m/e* (rel intensity) 336 (5.42), 334 (5.42), 255 (9.49), 254 (10.85), 222 (10.5), 220 (10.2), 158 (67.1), 140 (67.1), 128 (100).

***endo*-4-Hydroxytetracyclo[4.3.2.0^{2,9}.0^{3,5}]undeca-7,10-diene (5).** To a solution of 500 mg (1.48 mmol) of the bromotrifluoroacetate **3** in 25 mL of dry tetrahydrofuran, 85 mg (2.25 mmol) of sodium borohydride was added all at once. The solution was stirred vigorously at room temperature for 2 h under an inert atmosphere after which 15 1-mL portions of water were added over a period of 30 min. The solution was then poured into 150 mL of ethyl ether. The organic extract was washed with water (3 × 50 mL) and saturated sodium chloride solution (3 × 50 mL), and dried over anhydrous sodium sulfate. Evaporation of the solvent gave 177.6 mg (75%, crude) of the cyclopropanol product (**5**): IR (CCl_4) 3550, 3320, 2020, 2940, 2900, 1425, 1260, 1190, 1160, 1125, 912, 698 cm^{-1}; NMR ($CDCl_3$) δ 0.88 (2 H, multiplet), 2.37 (2 H, multiplet), 3.17 (1 H, triplet), 3.92 (4 H, broad multiplet), 5.70 (2 H, multiplet); mass spectrum (24 eV) *m/e* (rel intensity) 160 (1.5), 159 (18.2), 158 (50.3), 157 (19.9), 143 (7.9), 142 (8.5), 141 (23.6), 131 (28.2), 130 (56.9), 129 (100).

Synthesis of Deuterated Alcohol 5-*d*. A solution of 0.79 g (0.00236 mol) of **3** in 20 mL of dried tetrahydrofuran was stirred at 0 °C under an inert atmosphere for 10 min. Sodium borohydeuteride (0.277 g, 0.00663 mol) was added all at once. The heterogeneous solution was stirred for an additional 30 min at 0 °C. D_2O (0.5 mL) was syringed into the solution in 100-μL portions over a period of 30 min. The solution turned milky and hydrogen was evolved. The solution gradually turned gray after 20 min of stirring at ambient temperature. The solution was then transferred into 100 mL of cold water in small aliquots. The resulting aqueous solution was extracted with ethyl ether (5 × 75 mL). The organic phase was washed with 5% sodium hydroxide (3 × 100 mL), water (3 × 100 mL), and saturated sodium chloride solution (3 × 100 mL). Excess organic solvent was removed under a reduced pressure after drying over anhydrous sodium sulfate; 0.286 g of **5-*d*** was isolated, typical yield 75-77%.

Synthesis of Homobullvalenyl Mesylate 7. To a solution containing 0.1848 g (0.00115 mol) of **5** and 500 mg of triethylamine in 15 mL of anhydrous benzene-pentane (2:1) was added 360 mg of methanesulfonyl chloride in 50-μL aliquots over a period of 30 min at 0 °C under an inert atmosphere. After the reaction mixture turned chalky, the cold solution was allowed to warm to room temperature over a period of 2 h. The reaction mixture was then poured into 50 mL of cold water in small aliquots. The resulting solution was extracted with chloroform (6 × 50 mL). The organic extract was washed with 5% HCl (3 × 30 mL), 5% sodium bicarbonate (3 × 30 mL), and saturated sodium chloride solution (3 × 30 mL). The solution was dried over anhydrous sodium sulfate and concentrated under vacuum. Recrystallization of the crude product from ether/pentane (1:5) afforded 0.16 g of mesylate **7** (58%): NMR ($CDCl_3$) δ 1.20 (2 H, multiplet), 2.43 (3 H, multiplet), 3.07 (3 H, singlet), 3.91 (1 H, triplet, J = 7 Hz), 3.97 (4 H, multiplet), 5.73 (2 H, quartet, J = 9 Hz); IR (CCl_4) 3025, 2925, 1378, 1353, 1184, 992, 975, 936, 920, 891, 858, 708 cm^{-1}; mass spectrum (45 eV) *m/e* (rel intensity) 292 (99), 159 (100), 142 (89), 141 (81), 131 (81), 129 (89), 128 (73), 116 (64), 115 (84), 91 (93).

Anal. Calcd for $C_{12}H_{14}SO_3$: C, 60.481; H, 5.921; O, 20.142. Found: C, 60.38; H, 5.74; O, 20.05.

Solvolysis of 7 in Acetic Acid. A solution of 0.1 g of **7** and 0.04 g of sodium acetate in 5 mL of acetic acid (2:1) was sealed in a glass ampule and heated at 90 °C for 0.5 h. Analysis of the reaction mixture by GLC (SE-52 column at 130 °C) revealed the presence of a single new peak and <5% unreacted starting material. The crude reaction mixture was poured into 10 mL of ether and extracted with sodium bicarbonate (3 × 10 mL), water (2 × 10 mL), and saturated sodium chloride (2 × 10 mL). The organic phase was dried over anhydrous sodium sulfate and concentrated under vacuum to afford a crude oil. Preparative thin layer chromatography (silica-pentane/ether, 5:1) gave 35 mg of **8** (65% yield): IR (CCl_4) 3020, 2960, 2820, 1688, 1265 cm^{-1}; NMR ($CDCl_3$) δ 2.26 (2 H, m), 2.68 (2 H, d, J = 5 Hz), 2.95 (1 H, m), 3.6 (1 H, m), 5.7 (2 H, d), 6.1 (2 H, t, J = 5 Hz), 6.75 (1 H, t, J = 4 Hz), 9.27 (1 H, s), mass spectrum (70 eV) *m/e* (rel intensity) 160 (41.4), 143 (100), 131 (76.5).

An identical solvolysis of **7** in acetic-d_3 acid-d_1 afforded **8-*d***, NMR ($CDCl_3$) δ 6.75 (1 H, d, J = 4 Hz).

Reaction of 7 with Aluminum Trichloride. A solution of 50 mg (6.25 × 10^{-4} mol) of **7** and 82 mg (6.1 × 10^{-4} mol) of anhydrous aluminum trichloride in 25 mL of anhydrous ethyl ether was stirred at room temperature for 2 h. Water (10 mL) was added over 30 min and the organic phase was washed with 5% sodium bicarbonate (5 × 25 mL), water (3 × 25 mL), and saturated sodium chloride solution (2 × 50 mL). The solution was dried over anhydrous sodium sulfate and concentrated under vacuum to afford 38 mg of **8** which was identical in spectroscopic and chromatographic properties with **8** isolated from acetic acid solvolysis of **7**.

Synthesis of Homobullvalenyl Triflate 9. To a solution of 0.5 g of **5** in 10 mL of anhydrous pyridine was added 1.7 g of trifluoromethanesulfonyl anhydride over a period of 10 min in 0.5-g portions under an inert atmosphere at 0 °C. The resulting solution was allowed to stir for 2 h at 0 °C. The solution was poured into 50 mL of water which was extracted with ethyl ether (5 × 50 mL). The organic phase was washed with saturated sodium chloride solution (4 × 50 mL) and dried over anhydrous sodium sulfate. Evaporation of excess solvent under a reduced pressure and purification by preparative thin layer chromatography (silica/ether-pentane 1:5) afforded 0.9 g (99%) of the cyclopropyl triflate **9:** NMR ($CDCl_3$) δ 1.24 (2 H, multiplet), 2.4 (2 H, multiplet), 3.97 (4 H, multiplet), 3.95 (1 H, apparent triplet), 5.63 (2 H, multiplet); IR (CCl_4) 3030, 2960, 2940, 1425, 1210, 1155, 935, 920, 895, 865, 710, 650, 622 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 292 (0.1), 141 (14), 100 (16), 83 (35), 59 (base peak).

Synthesis of Deuterated Homobullvalenyl Triflate 9-*d*. The deuterated triflate **9-*d*** was prepared from **5-*d*** analogously to the preparation of **9** from **5**. Deuterium incorporation was 98%.

NMR ($CDCl_3$) δ 1.3 (2 H, triplet), 2.45 (2 H, multiplet), 3.94 (4 H, multiplet), 5.74 (2 H, multiplet); mass spectrum (70 eV) *m/e* (rel intensity) 293 (1.06), 160 (4.7), 142 (100), 143 (95.4), 129 (40.9).

Preparation of Dipotassium Azodicarboxylate. After 31 mL of 40% potassium hydroxide (by weight) solution was cooled to below 5 °C, 5 g of azodicarbonamide (Aldrich Chemical Co.) was added to the solution in small portions with stirring over a 2-h period. The temperature was kept below 8 °C during each addition. After stirring for an additional 1 h, the bright yellow dipotassium azodicarboxylate was filtered off using a Büchner funnel, and the solid was washed 20 times with 10 mL of precooled methanol (0 °C). Yields varied from 80 to 92% on several trials.

Diimide Reduction of 9. To a stirred suspension of 2.4 g (0.0123 mmol) of potassium azodicarboxylate and 0.72 g (0.00246 mmol) of **9** in 15 mL of methanol, 500 mg of acetic acid in 2 mL of methanol was added over a period of 1 h. The reaction mixture was stirred at room temperature for 30 min. The reaction mixture was diluted with water and extracted with pentane. The pentane extract was washed with saturated sodium chloride solution (3 × 50 mL) and dried over anhydrous sodium sulfate. Evaporation of excess solvent followed by thin layer chromatography (silica/ether-pentane, 1:8) afforded 20% of **11** and 51% of **10**.

11: NMR δ 4.5 (1 H, triplet, J = 7 Hz), 1-2.8 (14 H, multiplet); IR 2990, 2920, 2860, 1420, 1237, 1200, 1145, 975, 900 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 296 (14.7), 163 (73.5), 147 (32.3), 146 (100).

10: NMR δ 5.7 (2 H, multiplet), 4.5 (1 H, triplet, J = 7 Hz), 1.2-2.8 (10 H, multiplet); IR 3020, 2990, 2924, 2860, 970, 910, 885 cm^{-1}; mass spectrum (70 eV) *m/e* (rel intensity) 294 (21.6), 161 (100), 145 (56.6), 144 (60).

Reaction of Aluminum Trichloride with 5. A solution of 50 mg (6.25 $\times 10^{-4}$ mol) of crude **5** and 82 mg (6.1 $\times 10^{-4}$ mol) of anhydrous aluminum trichloride in 25 mL of anhydrous ethyl ether was allowed to stir for 2 h. Water (10 mL) was then added over a period of 30 min. The organic phase was separated and washed with 5% sodium bicarbonate (5 $\times$ 25 mL), water (3 $\times$ 25 25 mL), and saturated sodium chloride solution (2 $\times$ 50 mL), and dried over anhydrous sodium sulfate. Evaporation of excess solvent gave 0.38 mg of **8.** Purification of **8** could be achieved by thin layer chromatography (silica/ether-pentane, 1:8): IR (CCl_4) 3020, 2960, 2820, 1688, 1265 cm^{-1}. NMR, see text; mass spectrum (70 eV) *m/e* (rel intensity) 160 (41.4), 143 (100), 131 (76.5).

Preparative Solvolysis of Triflate 9. A solution of 0.48 g (0.00164 mol) of **9** in 60 mL of 40% aqueous acetone (v/v) buffered with 0.05 M 2,6-lutidine was degassed in a combustion tube for a period of 1 h. The tube was cooled to -78 °C and sealed under vacuum. The reaction mixture was then allowed to warm to room temperature and then slowly warmed to 95 °C and maintained at that temperature for 3 h. The reaction mixture was then cooled to 0 °C and poured into 50 mL of cold water. The acetone was removed under a reduced pressure and the resulting aqueous solution was extracted with ethyl ether (5 $\times$ 70 mL). The organic phase was washed with water (3 $\times$ 50 mL) and saturated sodium chloride solution and dried over anhydrous sodium sulfate. Evaporation of excess solvent afforded 0.181 g (69%) of alcohols **12** and **13** (17:83). Identification of alcohols **12** and **13** was made possible via Sarett oxidation to afford the two known ketones **14** and **15.** Alcohol **12** could be separated from the crude reaction mixture by crystallization from ethyl ether-carbon tetrachloride (1:5) and subsequent thin layer chromatography (silica/pentane-ether, 5:2). Solvolysis of **9-*d*** under identical conditions gave **12-*d*** and **13-*d***.

12-*d*: ^{1}H NMR (CCl_4) δ 3.4 (m, 0.88 H), 3.5 (m, 0.86 H), 4.25 (m, 0.94 H), 5.4 (1.81 H), 5.7 (m, 5.50 H). Integral intensities ($\pm$0.05) are normalized to ten protons.

Sarett Oxidation of Alcohols 12-*d* and 13-*d*. Chromic anhydride (0.30 g) was added to a stirred solution of 4.7 mL of pyridine and 35 mL of methylene chloride. The resulting burgundy colored solution was allowed to stir for 15 min. A solution of **12-*d*** and **13-*d*** (0.185 g, 0.00115 mol) in 5 mL of methylene chloride was added in small aliquots over a period of 5 min. The solution, which turned black upon addition of alcohols, was allowed to stir for 20 min. Isopropyl alcohol (5 mL) was added and the resulting solution was added to 50 mL of cold water. The aqueous solution was extracted with ethyl ether (10 $\times$ 25 mL). The organic phase was washed with 5% sodium hydroxide solution (3 $\times$ 35 mL), 5% hydrochloric acid (3 $\times$ 25 mL), water (3 $\times$ 35 mL), and saturated sodium chloride solution (3 $\times$ 40 mL), and dried over anhydrous sodium sulfate. Evaporation of excess solvent under reduced pressure and thin layer chromatographic purification (silica/pentane-ether, 5:1) of the crude product afforded 120 mg of ketones **15** (82.6%) and **14** (17.35%). **15:** NMR, see text.

Solvolysis of Compounds 9, 10, and 11 in Acetic Acid. A solution of 0.1 g of the triflate (**9**, **10**, or **11**) and tetradecane (0.01 M) in 10 mL of acetic acid buffered with sodium acetate (0.1 M) was pipetted into a series of capillary tubes. Six tubes were sealed and immersed in an oil bath at 100.0 $\pm$ 0.2 °C. Samples were quenched at various time intervals by rapid cooling to -78 °C followed by aqueous workup. The rates of disappearance of the triflates **9**, **10**, and **11** were then analyzed by analytical GLC (column, 3% SE-30, 125 °C) over a period of 4 h (>2 half-lives). The logarithms of the normalized areas vs. 0.01 M tetradecane of the triflates were plotted vs. time and the slope of these plots determined by least-squares analysis (correlation coefficient $\geq$0.960). Product analyses were determined by observing the appearance of product acetates in the same GLC runs.

Determination of the Rate of Solvolysis of 9 in Aqueous Acetone. A solution of 0.1 g of triflate **9** and 0.01 M tetradecane in 30 mL of 40% aqueous acetone buffered with 0.05 M 2,6-lutidine was sealed under vacuum in a series of capillary tubes. The tubes were immersed in an oil bath at temperatures ranging from 70 to 95 $\pm$ 0.2 °C. Samples were quenched at various time intervals by rapid cooling to -78 °C, followed by aqueous workup. The rates of disappearance of the triflate **9** were determined as above by analytical GLC (3% SE-30, 125 °C). All runs were followed over at least 2 half-lives (correlation coefficient $\geq$0.960). Product analyses were determined by GLC vs. authentic **12** and **13.**

Calculation of Deuterium Satellite Intensity Ratios (*D*). From the mass spectrum of **9** (*m/e* (rel intensity) 293 (14.4), 292 (100), 291 (4.0)) and that of **9-*d*** (294 (14.9), 293 (100), 292 (5.96)), **9-*d*** was determined to be 98% d_1. Likewise, from the mass spectra of **15** (159 (11.5), 158 (100), 157 (19.8)) and **15-*d*** (160 (12.0), 159 (100), 158 (34.2), 157 (5.9)), **15-*d*** was determined to be 87% d_1, 13% d_0. The expected deuterium satellite intensity ratio for H_a in **15-*d*** (D_a) for the case of statistical scrambling was calculated as follows. The intensity of the parent resonance $I_H{}^a = 1 - 3\,(0.87/10) = 0.739$ and the intensity of the deuterium satellite resonance $I_D{}^a = 2\,(0.87/10) = 0.174$. $D_a = I_D{}^a/I_H{}^a = 0.174/0.739 = 0.24$. The value of D for other positions and distributions was calculated similarly.

Experimental deuterium satellite intensity ratios for **15-*d*** were determined by digital integration of the ^{1}H NMR spectrum of **15-*d*** (Figure 2) from inflection to inflection. For the resonances due to H_c, H_e, H_f, and H_i, in which the satellite peaks are incompletely resolved, intensity ratios determined by digital integration were compared to computer-simulated composite spectra for various possibilities. Figure 3 illustrates such a comparison for H_c and H_e for the cases of 9-fold (D = 0.12) and 11-fold (D = 0.24) scrambling. Second-order factors in line intensities are specifically accounted for by this procedure.

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