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Conformational Effects on Acetolysis of Bicyclo[3.2.0]hept-6-en-2-yl and Bicyclo[3.2.0]hept-2-yl Derivatives. Homoallylic Participation vs. σ Participation[1]

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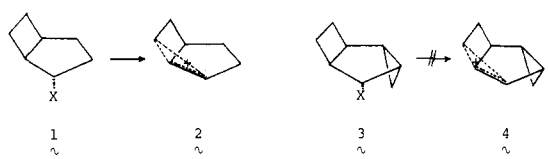
Abstract: The acetolysis reactions of *anti,exo-* and *anti,endo*-tricyclo[5.2.0.0^{2,5}]non-3-en-6-yl tosylates (**7** and **8**), *anti*-tricyclo[5.2.0.0^{2,5}]non-6-yl tosylate (**9**), and *syn,exo,exo-* and *syn,exo,endo*-tetracyclo[5.4.0.0^{2,5}.0^{8,11}]undeca-3,9-dien-6-yl tosylates (**10** and **11**) have been studied to obtain a direct insight into anchimeric assistances by cyclobutane and cyclobutene rings. As important factors to influence the reactivity of the tosylates, homoallylic and σ participations, inductive effect, and conformational change have been discussed. The homoallylic participation (**33**) is more effective for stabilization of the transition state than the σ participation (**34**) ($\Delta\Delta G^{\ddagger}$ = ca. 1.1 kcal/mol at 25 °C) in contrast to the result in the bicyclic system. The ordering of anchimeric stabilization by small-ring compounds in a similar geometrical system is estimated to be cyclopropane (700) > cyclobutene (7) > cyclobutane (1.0). The acetolysis product studies also support the importance of anchimeric assistances by cyclobutene and cyclobutane.

Solvolysis studies of small-ring compounds have long intrigued organic chemists because of their unique properties caused by conjugative interaction between a strained bonding orbital and an adjacent carbonium ion. Although solvolysis reactions of cyclopropylcarbinyl derivatives have been extensively investigated,[2,3] much less attention has been given to those of cyclobutylcarbinyl derivatives.[4] An original work about cyclobutylcarbinyl derivatives was carried out by Winstein and co-workers[4a] in solvolysis of bicyclo[3.2.0]heptyl *p*-bromobenzenesulfonate (**1**), suggesting the stabilized carbonium ion (**2**) by the cyclobutane (σ participation). The



1 2 3 4

molecular orbital calculations have also provided some evidence for the stabilizing effects by cyclobutane rings.[5] Paquette and co-workers,[3e] however, have suggested that anchimeric assistance by the cyclobutane (**4**) is not significant, when compared to that by the cyclopropane, in the solvolysis of the tricyclo[4.2.0.0^{2,4}]oct-5-yl derivative (**3**) which is partially similar to **1**.

Recently cyclobutenylcarbinyl cation **6**, which is stabilized by the double bond (homoallylic participation), has received a considerable amount of attention.[6] However, when one compares the rate of solvolysis of *exo*-bicyclo[3.2.0]heptenyl derivative **5** to that of **1**, both the rates are essentially identical[6e]

5 6

in spite of the fact that their transition states are quite different. Here questions arise as to whether the σ participation and the π participation are in nature significant in solvolysis of **1** and **5** and, if any, to what extent they are important as compared to a model compound.

In order to obtain direct insight into the above questions one has to investigate solvolysis reactions of the bicyclo[3.2.0]-heptenyl and bicyclo[3.2.0]heptyl derivatives in a rigid ring system eliminating complications due to conformational factors.[6f] Thus, we undertook to synthesize *anti,exo-* and *an-*

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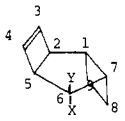
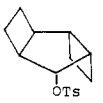
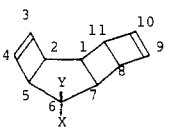
ti,endo-tricyclo[5.2.0.0^{2,5}]non-3-en-6-yl tosylates (**7** and **8**), respectively, *anti*-tricyclo[5.2.0.0^{2,5}]non-6-yl tosylate (**9**), and



7, Y=H, X=OTs
8, Y=OTs, X=H



9

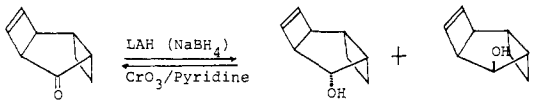


10, Y=H, X=OTs
11, Y=OTs, X=H

syn,exo,exo- and *syn,exo,endo*-tetracyclo[5.4.0.0^{2,5}.0^{8,11}]-undeca-3,9-dien-6-yl tosylates (**10** and **11**), respectively, and we have investigated their acetolysis reactions.

Results

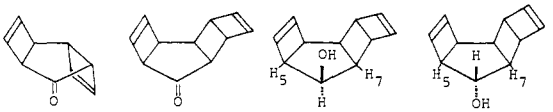
Sodium borohydride reduction of tricyclo[5.2.0.0^{2,5}]non-3-en-6-one (**12**)[7] gave a mixture of *anti,exo*-tricyclo-[5.2.0.0^{2,5}]non-3-en-6-ol (**13**, 4.1%) and *anti,endo*-tricyclo[5.2.0.0^{2,5}]non-3-en-6-ol (**14**, 77.9%), whereas lithium



12 13 14

aluminum hydride reduction increased the yield of **13** (11.3%) approximately three times. The same skeleton of **13** and **14** was confirmed by formation of **12** from oxidation of these alcohols with chromium trioxide–pyridine. After **13** and **14** were separated by chromatography on a silica gel column, their relative stereochemistries were assigned on the basis of their IR spectra for an intramolecular hydrogen bond between the hydroxy group and the double bond.[8] The endo epimer (**14**) showed a doublet absorption at 3637 (free OH) and 3617 cm^{-1} (-OH···π), whereas the exo epimer (**13**) showed a singlet absorption at 3639 cm^{-1} (free OH).[9] These alcohols were converted to corresponding tosylates **7** and **8** in the usual fashion. The saturated tosylate (**9**) was prepared by sodium borohydride reduction of its corresponding ketone which was obtained from hydrogenation of *anti*-tricyclo[5.4.0.0^{2,5}]nona-3,9-dien-6-one (**15**)[7] followed by esterification.

Sodium borohydride reduction of tetracyclo[5.4.0.0^{2,5}.0^{8,11}]undeca-3,9-dien-6-one (**16**)[6f] yielded stereospecifically *syn,exo,endo*-tetracyclo[5.4.0.0^{2,5}.0^{8,11}]undeca-3,9-dien-6-ol (**17**). The exo epimer (**18**) was obtained by



15 16 17 18

inversion of **11** with tetra-*n*-butylammonium acetate in dry acetone,[10] followed by lithium aluminum hydride reduction. Geometrical assignments of **17** and **18** were based upon their NMR spectra. The methine proton of **18** appeared at δ 3.82 with a singlet absorption while that of **17** appeared at δ 4.34 with a triplet (J = 8.0 Hz). This observation was easily explained by the dihedral angles of the methine proton with H_5 and H_7. These coupling data were also in good agreement with those reported for tricyclo[4.2.0.0^{2,4}]oct-5-yl derivatives.[3e]

Rates of acetolysis were measured by the UV absorbance method.[6b] The reactions displayed good first-order behavior until at least 2 half-lives except acetolysis of **9**, in which the initial rates were measured because of formation of an internal returned product. The kinetic data are summarized in Table I along with those for the related compounds.

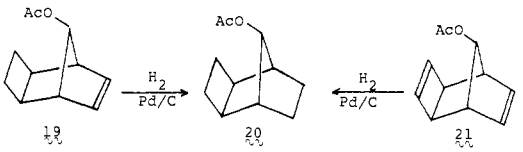
Acetolysis of **7** gave rise to *exo,syn*-tricyclo[4.2.1.0^{2,5}]-non-7-en-9-yl acetate (**19**) in 81% yield, of which structure was assigned on the basis of a chemical reaction and its NMR

Table I. Kinetic Data for Acetolyses of Tosylates

substrate[a]	temp, °C[b]	k, s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
7	17	(1.12 ± 0.01) × 10^{-4} [c]		
	25	(3.48 ± 0.04) × 10^{-4} [c]	23.4	+4.2
8	25	(2.37 ± 0.03) × 10^{-5} [c]	22.6	−4.0
	50	(4.90 ± 0.01) × 10^{-4} [c]		
9	25	(5.24 ± 0.11) × 10^{-5} [c]	21.4	−6.5
	50	(9.25 ± 0.47) × 10^{-4} [c]		
10	17	(5.18 ± 0.02) × 10^{-5} [c]		
	25	(2.01 ± 0.03) × 10^{-4} [c]	28.1	+19.0
11	75	(9.79 ± 0.03) × 10^{-5} [c]		
	100	(9.55 ± 0.05) × 10^{-4} [c]		
	25	3.54 × 10^{-7} [d]	22.4	−12.5
32	25	1.97 × 10^{-4} [e]	25.2	+9.0
35	25	6.19 × 10^{-4} [f]	24.6	+9.4

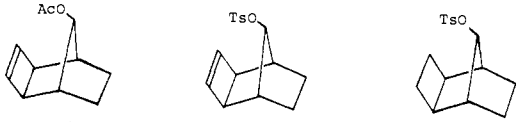
[a] Ca. 0.02 M in acetic acid buffered with 0.045 M sodium acetate. [b] ±0.1 °C. [c] The errors are deviation from the average of two runs. [d] Extrapolated value. [e] Reference 6b. [f] Reference 6f.

spectrum. Hydrogenation of **19** in the presence of palladium on carbon led to the same product (**20**) as obtained from hydrogenation of the known acetate (**21**).[6b] Furthermore, a



19 20 21

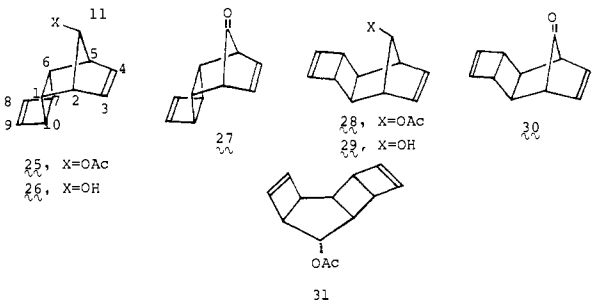
characteristic triplet (2 H, J = 2.0 Hz) observed for the vinyl protons indicated an *anti*-7-norbornenyl structure.[11] On the other hand, acetolysis of **8** gave a mixture of **19** (70%), **22** (4%), and **23** (19%) (an internal returned product). After hydrogenation of **22** and **23**, their structures were established by NMR



22 23 24

spectral comparison with those of **20** and **24**. Acetolysis of **9** gave a mixture of **20** (20%) and **24** (66%) (an internal returned product) as expected from the result of **1**.[4a]

The exo tetracyclic tosylate (**10**) yielded *endo,exo,syn*-tetracyclo[4.4.1.0^{2,5}.0^{7,10}]undeca-3,8-dien-11-yl acetate (**25**), of which structure and configuration were assigned by the NMR spectral data of **25**, **26**, and **27**, comparing with those of **28**, **29**, and **30**.[6f] Since the peaks of H_1 (H_6), H_2 (H_5), and



25, X=OAc
26, X=OH
27
28, X=OAc
29, X=OH
30
31

Table II. Vicinal Coupling Constants in ^1H NMR Spectra, Dihedral Angles, and Estimated Conformations of Tosylates

substrate	coupling constants, Hz	dihedral angles, deg	conformation
7	1.5, 8.0[a]	116, 9	planar
8	4.0, 7.6[a]	132, 16	planar
9	3.6, 7.2[a]	129, 20	planar
10	0.0[b]	100, 100	slightly boat
11	8.0[c]	9, 9	planar
37	2.5[d]	100, 54	boat
38	2.4[d]	100, 56	boat

[a] Two doublets. [b] Singlet. [c] Triplet. [d] Doublet.

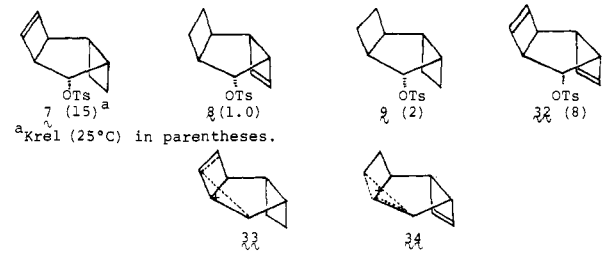
H_{10} (H_7) protons of **25** were not resolved, the NMR spectrum of the corresponding alcohol (**26**), which was obtained by lithium aluminum hydride reduction of **25**, was measured in the presence of $Eu(dpm)_3$ showing a spin–spin interaction between H_1 and H_2 by the double resonance study. Thus **25** was assigned to have the endo orientation of the cyclobutane to the norbornene ring because such interaction was not observed for the exo orientation.[6f] Furthermore, the same chemical shift of H_3 and H_4 protons (δ 6.45) of **27** and **30** indicated the exo orientation of the cyclobutene in **27** since, if it was in the endo, the protons (H_3 and H_4) should appear at higher magnetic field owing to the long-range shielding effects by the other double bond.[12] This structural assignment might also be supported by no observation of a photochemical conversion of **25** to homopentaprismane derivative.[13] The selective hydride reduction[14] of **27** to **26** and a characteristic triplet peak of H_3 and H_4 protons on the NMR spectrum of **26**[15] indicated the syn isomeric structure of the hydroxy group to the cyclobutane. The endo tosylate (**11**) produced a mixture of **25** (55%), epimeric acetate **31** (20%), and two unidentified products (11 and 6%).

Discussion

In order to evaluate the importance of anchimeric assistance by rate comparisons, one has to choose a right model compound of which gross structures are similar to those of the compounds to be examined. Thus, the conformations of **7, 8, 9, 10, 11,** and **37** were estimated by the measurement of the coupling constants of their methine protons, followed by calculation of the corresponding dihedral angles using the Karplus equations.[16] Table II shows that **7, 8, 9,** and **11** are approximately in a similar structure with a planar cyclopentane. The bicyclic tosylates (**38** and **37**[17]), however, are in a "boat" conformation and **10** seems to be in a slightly "boat" structure.[18] Taking this into consideration we will discuss the acetolysis reactivity of these tosylates (Table I).

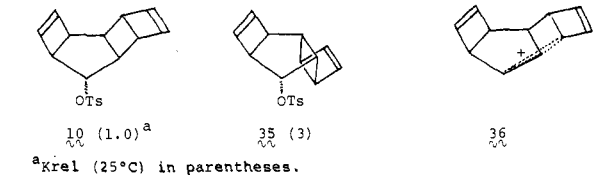
The rate ratios of **7**/**9** (7) and **32**/**8** (8) at 25 °C clearly indicate that *the homoallylic participation* (**33**) *is more effective for stabilization of the transition state than the σ participation* (**34**) ($\Delta\Delta G^{\ddagger}$ = ca. 1.1 kcal/mol) in contrast to the observation in the bicyclic system.[6e] A factor of 2 which is obtained from the rate ratio of **9**/**8** or **7**/**32** indicates that inductive rate retardation by the double bond[6f,19] influences the transition states of both the participations in a similar way. Thus, the exo/endo rate ratio (**7**/**8** = 15) must be due to a combination of difference of the participations (7.5) and the rate retardation of **8** (2).

In the tetracyclic system, **10** is three times less reactive than **35**[6f] indicating that the σ participation (**36**) has little effect on the reactivity of **10**. This is in accord with the product study which will be discussed later. The exo/endo rate ratio of **10**/**11** (570) may be explained by a combination of the homoallylic



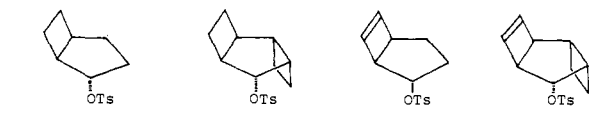
[a] k_{rel} (25 °C) in parentheses.

participation (a major factor) and difference of their ground-state strains.[3e]

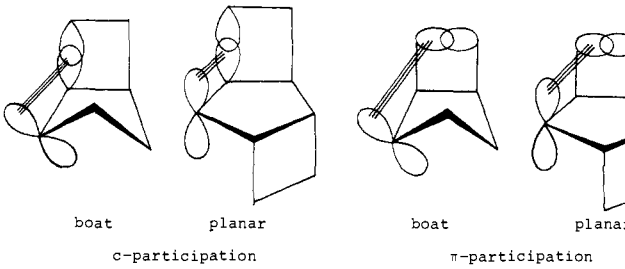


[a] k_{rel} (25 °C) in parentheses.

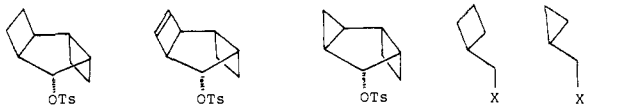
The conformational effects on the reactivity can be derived from the rate comparisons of **37**[6e] and **38**[6d] with **9** and **7**. The rate ratios of **9**/**37** (5) and **7**/**38** (36) reveal that the homoallylic participation is more sensitive to the conformational change from boat to planar than the σ participation by a difference of the transition state free energy of approximately 1.3 kcal/mol. This different stabilization must be due to the different proximity between the reaction center and bonding orbital which is used for participation since the steric factors seem to be similar for both systems. The homoallylic participation exists across one intervening carbon atom[20] while the σ participation interacts with the adjacent carbon atom. Thus, it is reasonable to conclude that the difference of conformation makes more influence on the transition state of the homoallylic participation than that of the σ participation. In both cases, however, the planar structure provides a good orientation for the interaction of the p orbital of the cation with the σ or π bonding orbital.



[a] k_{rel} (50 °C) in parentheses.



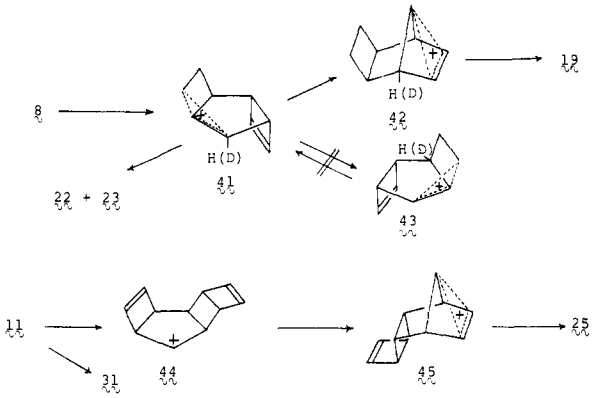
It is of some interest to estimate the neighboring stabilization effects of cyclobutane, cyclobutene, and cyclopropane in a similar geometrical system. Thus, the rates of **9** and **7** were compared with that of **3**[3e] which undergoes solvolysis through cyclopropyl participation. A rate enhancement of **3** (700), when compared to **9**, must be due to formation of the stable bishomoallylic carbonium ion and relief of its ring strain (33.5 kcal/mol).[21] However, the latter factor may not be important since a rate ratio of **40**/**39** (1000)[22] in a flexible system is somewhat larger than that of **3**/**9**. Consequently, *the ordering of effectiveness of these neighboring groups is estimated to be cyclopropane (700) > cyclobutene (7) > cyclobutane (1.0).* The present findings further confirm the reactivity order of cyclopropylcarbinyl and cyclobutylcarbinyl derivatives reported by Paquette and co-workers.[3e]



9 (1.0)[a] 7 (7) 3 (700) 39 (1.0) 40 (10^3)

[a]Krel (25°C) in parentheses.

The stereospecific rearrangements of **7** and **10** in acetolysis to **19** and **25**, respectively, through a well-known path[6] support involvement of the homoallylic participation in the transition states. Acetolysis of **8** produces initial stabilized carbonium ion **41** by the σ participation which leads to **19** by way of **42** and partially to **22** and **23**. The NMR spectral study of the acetate (**19**) from the deuterium-labeled tosylate (**8**-*6-d*) shows no distribution of the deuterium[23] indicating that a rapid equilibrium between **41** and **43**, as expected from solvolysis of the



bicyclic system (**1**),[4b] is not involved. The discrepancy may be explained by the greater stability of **42** compared to **43**. Consequently **41** rearranges to **42** without the equilibrium stage between **41** and **43**.

On the other hand, **11** leads predominantly to **25** through a classical carbenium ion (**44**) rearranging to an *anti*-7-norbornenyl carbonium ion (**45**), and to **31** by attack of solvent. A thermal rearrangement of **31** to **25** is removed by examination of the stability of **31** under the acetolysis condition.

Experimental Section

Melting points were taken on a Yamato MP-21 melting point apparatus and are uncorrected. Infrared spectra were recorded on a Shimadzu IR-400 spectrophotometer and ultraviolet spectra were determined with a Shimadzu UV-200 spectrophotometer. Nuclear magnetic resonance spectra were recorded using a Hitachi R-24 instrument with the chemical shifts (δ) given in parts per million down from Me_4Si. Gas–liquid chromatography was performed on a Shimadzu GC-4B instrument. Microanalyses were determined in the microanalytical laboratory of the Institute of Physical and Chemical Research, Wako-shi, Satitama, Japan.

***anti,exo*- and *anti,endo*-Tricyclo[5.2.0.0^{2,5}]non-3-en-6-ols (13 and 14).** **A.** To a solution of **12**[7] (5.0 g, 37.3 mmol) in 100 mL of methanol was added 1.4 g (37.3 mmol) of sodium borohydride at 0 °C. The resulting solution was allowed to stir at room temperature for 24 h. After addition of 100 mL of saturated sodium chloride solution, the resulting solution was extracted with ether three times. The ethereal solution was washed with saturated sodium chloride solution once, dried ($MgSO_4$), and concentrated under vacuum to give a mixture of **13** and **14**, which was separated by chromatography on a silica gel column eluting with 30% ether in hexane to produce 210 mg (4.1%) of **13** and 3.9 g (77.9%) of **14**. **13:** mp 39.0–40.0 °C; IR (KBr) 3230 (OH), 3050, 2980, 2920, 2900, 2850, 1560, 1100, 1030, 800, and 740 cm^{-1}; NMR (CCl_4) δ 6.05–5.85 (m, 2 H, vinyl), 4.10 (d, 1 H, J = 7.5 Hz, methine), 3.38 (d, 1 H, J = 3.2 Hz), 3.05 (d, 1 H, J = 3.2 Hz), 2.95 (s, 1 H, OH), and 2.85–1.65 (m, 6 H). Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 78.90; H, 8.79. **14:** IR (film) 3340 (OH), 3040, 2940, 2870, 1564, 1080, 810, 790, and 760 cm^{-1}; NMR (CCl_4) δ 6.14 (d, 1 H, J = 3.0 Hz, vinyl), 6.00 (d, 1 H, J = 3.0 Hz, vinyl), 4.23 and 4.10 (2 d, 1 H, J = 4.0, 7.5 Hz, methine), 3.57 and 3.45 (2 d, 1 H, J = 3.5 Hz), 2.94 (d, 1 H, J = 3.5 Hz), and 2.80–1.50 (m, 7 H). Anal. Calcd for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.41; H, 8.74.

B. To a suspention of 148 mg (3.9 mmol) of lithium aluminum hydride in 20 mL of anhydrous ether at 0 °C was added dropwise a solution of **12** (400 mg, 3.0 mmol) in 10 mL of ether. The resulting mixture was allowed to stir at room temperature for 18 h. Ether extraction, followed by chromatography on a silica gel column, gave a mixture of **13** (45 mg, 11.3%) and **14** (283 mg, 70%).

***anti,exo*-Tricyclo[5.2.0.0^{2,5}]non-3-en-6-yl Tosylate (7).** To a solution of **13** (94 mg, 0,69 mmol) in 15 mL of pyridine was added 264 mg (1.38 mmol) of *p*-toluenesulfonyl chloride at −10 °C. The resulting solution was allowed to stand in a refrigerator for 7 days. Then the solution was poured onto 20 g of ice and extracted with ether three times. The ethereal solution was washed with saturated sodium chloride solution twice, dried ($MgSO_4$), and concentrated under reduced pressure to produce a pale pinkish liquid, which was crystallized from hexane to yield 105 mg (52%) of **7:** mp 58.0–59.5 °C; IR (KBr) 3060, 2980, 2950, 1600, 1566, 1370, 1350, 1190, 1170, 910, 820, 745, and 665 cm^{-1}; NMR (CCl_4) δ 7.68 and 7.22 (2 d, A_2B_2, 4 H, J = 8.0 Hz, aromatic), 5.88 (s, 2 H, vinyl), 4.80 and 4.68 (2 d, 1 H, J = 1.5, 8.0 Hz, methine), 3.48 (2 d, 1 H, J = 1.5, 3.0 Hz), 3.08 (d, 1 H, J = 3.0 Hz), 2.45 (s, 3 H, CH_3–), and 2.90–1.50 (m, 6 H). Anal. Calcd for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25. Found: C, 66.31; H, 6.29.

***anti,endo*-Tricyclo[5.2.0.0^{2,5}]non-3-en-6-yl Tosylate (8).** To a solution of **14** (2.1 g, 15.4 mmol) in 30 mL of pyridine was added 4.4 g (23.1 mmol) of *p*-toluenesulfonyl chloride at −10 °C. The resulting solution was allowed to stand for 4 days. The mixture was poured onto 150 g of ice with 5 mL of concentrated hydrochloric acid. The same workup procedure as mentioned for **7** gave 3.6 g (82%) of **8:** mp 49.5–50.0 °C; IR (KBr) 3070, 2980, 1600, 1566, 1356, 1190, 1180, 960, 840, 815, and 670 cm^{-1}; NMR (CCl_4) δ 7.68 and 7.22 (2 d, A_2B_2, 4 H, J = 8.0 Hz, aromatic), 5.92 (s, 2 H, vinyl), 4.86 and 4.72 (2 d, 1 H, J = 4.0, 7.6 Hz, methine), 3.60 and 3.48 (2 d, 1 H, J = 2.7, 7.6 Hz), 2.91 (d, 1 H, J = 2.7 Hz), 2.39 (s, 3 H, CH_3–), and 2.85–1.30 (m, 6 H). Anal. Calcd for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25. Found: C, 66.06; H, 6.28.

***anti*-Tricyclo[5.2.0.0^{2,5}]non-6-yl Tosylate (9).** Tricyclo[5.2.0.-0^{2,5}]nonan-6-one (410 mg, 3.0 mmol) was reduced with sodium borohydride (76 mg, 2 mmol) in 15 mL of methanol to give 359 mg (86%) of the corresponding alcohol, which was converted to **9** (426 mg, 56%) by the above described procedure: mp 46.0–47.0 °C; IR (KBr) 3075, 3060, 2950, 1600, 1350, 1185, 1175, 1095, 860, 810, and 660 cm^{-1}; NMR (CCl_4) δ 7.68 and 7.24 (2 d, A_2B_2, 4 H, J = 8.0 Hz, aromatic), 4.92 and 4.85 (2 d, 1 H, J = 3.6, 7.2 Hz, methine), 2.41 (s, 3 H, CH_3–) and 3.30–1.05 (m, 12 H). Anal. Calcd for $C_{16}H_{20}O_3S$: C, 66.18; H, 6.89. Found: C, 65.83; H, 6.94.

***syn,exo,endo*-Tetracyclo[5.4.0.0^{2,5}.0^{8,11}]undeca-3,9-dien-6-ol (17).** To a solution of **16**[6f] (458 mg, 2.9 mmol) in 30 mL of methanol was added sodium borohydride (55 mg, 1.5 mmol) at room temperature. The resulting solution was allowed to stir overnight. After addition of water, ether extraction gave 407 mg (88%) of **17:** mp 75.0–76.5 °C; IR (KBr) 3360 (OH), 3040, 2940, 1300, 1145, 1075, 950, 915, 850, 740, and 710 cm^{-1}; NMR (CCl_4) δ 6.30 (m, 4 H, vinyl), 4.34 (t, 1 H, J = 8.0 Hz, methine), 3.69–2.60 (m, 6 H), and 2.36–2.02 (m, 1 H). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.34; H, 7.60.

***syn,exo,endo*-Tetracyclo[5.4.0.0^{2,5}.0^{8,11}]undeca-3,9-dien-6-yl Tosylate (11).** To a solution of **17** (376 mg, 2.4 mmol) in 11 mL of pyridine was added *p*-toluenesulfonyl chloride (483 mg, 2.5 mmol) at −16 °C. The resulting solution was allowed to stand in a refrigerator for 10 days. The mixture was poured onto 60 g of ice and extracted with ether three times. The ethereal solution was washed with water several times, dried ($MgSO_4$), and evaporated to give 474 mg (64%) of **11:** mp 91.0–92.5 °C; IR (KBr) 3040, 2960, 1595, 1490, 1365, 1170, 1095, 985, 925, 890, 865, 830, and 660 cm^{-1}; NMR (CCl_4) δ 7.73 and 7.24 (2 d, A_2B_2, 4 H, J = 8.1 Hz, aromatic), 6.27 (m, 2 H, vinyl), 6.04 (m, 2 H, vinyl), 4.91 (t, 1 H, J = 8.0 Hz, methine), 3.70–2.58 (m, 5 H), 2.48 (s, 3 H, CH_3–), and 2.14 (m, 1 H). Anal. Calcd for $C_{18}H_{18}O_3S$: C, 68.76; H, 5.77. Found: C, 68.66; H, 5.79.

***syn,exo,exo*-Tetracyclo[5.4.0.0^{2,5}.0^{8,11}]undeca-3,9-dien-6-yl Acetate (31).** A solution of **11** (442 mg, 0.30 mmol) in 70 mL of tetra-*n*-butylammonium acetate–acetone solution (0.09 g in 1 mL of acetone) was allowed to stir at 55 °C for 20 h.[10] After addition of water, ether extraction gave 278 mg (98%) of crude acetate **31.** The analytical sample was purified by chromatography on a silica gel column eluting

with 7.5% ether in pentane. **31:** IR (film) 3040, 2950, 1730 (>C=O), 1372, 1236, 1018, 969, 756, and 730 cm^{-1}; NMR (CCl_4) δ 6.32 (m, 3 H, vinyl), 6.12 (m, 1 H, vinyl), 4.71 (s, 1 H, methine), 3.66-3.30 (m, 2 H), 3.16-2.22 (m, 4 H), and 1.93 (s, 3 H, CH_3-). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.11; H, 7.01.

***syn,exo,exo*-Tetracyclo[5.4.0.$0^{2,5}$.$0^{8,11}$]undeca-3,9-dien-6-yl Tosylate (10).** Acetate **31** (267 mg, 1.3 mmol) was reduced with lithium aluminum hydride (201 mg, 5.3 mmol) in 60 mL of ether at room temperature for 13 h. Ether extraction gave 190 mg (90%) of **18** as a liquid: NMR (CCl_4) δ 6.27 (m, 3 H, vinyl), 6.03 (m, 1 H, vinyl), 3.82 (s, 1 H, methine), 3.64-3.27 (m, 2 H), and 3.14-2.22 (m, 5 H).

This alcohol (190 mg, 1.2 mmol) was converted to **10** as mentioned above yielding 196 mg (53%): mp 76.5-77.5 °C; IR (KBr) and 3040, 2960, 1600, 1500, 1350, 1180, 1096, 920, 905, 820, 760, and 680 cm^{-1}; NMR (CCl_4) δ 7.57 and 7.14 (2 d, A_2B_2, 4 H, J = 8.1 Hz, aromatic), 6.17 (m, 3 H, vinyl), 5.95 (m, 1 H, vinyl), 4.54 (s, 1 H, methine), 3.61-3.29 (m, 2 H), 3.11-2.70 (m, 3 H), and 2.63-2.19 (m, 4 H). Anal. Calcd for $C_{18}H_{18}O_3S$: C, 68.76; H, 5.77. Found: C, 68.53; H, 5.80.

Kinetic Measurements. The rates were measured as previously described.[6b] The kinetic data are shown in Table I.

Preparative Acetolysis of 7. A solution of **7** (22.0 mg) in 2.6 mL of acetate buffer in a sealed tube was heated at 25 °C for 5 h. The cooled solution was neutralized with sodium bicarbonate and extracted with ether three times. The ethereal solution was washed with water twice, dried ($MgSO_4$), and evaporated to give crude product, which was purified by chromatography on a silica gel to yield 11 mg (81%) of **19:** IR (film) 3130, 3060, 2980, 2860, 1740 (>C=O), 1360, 1240, 1215, 1200, 1050, and 740 cm^{-1}; NMR (CCl_4) δ 5.87 (t, 2 H, J = 2.0 Hz, vinyl), 4.30 (s, 1 H, methine), 2.90-2.70 (m, 2 H), and 2.40-1.72 (m, 9 H). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.13; H, 7.90.

Preparative Acetolysis of 8. A solution of **8** (258 mg) in 25 mL of acetate buffer in a sealed tube was heated at 25 °C for 120 h. The similar workup procedure, as mentioned above, gave a mixture of **19** (90 mg, 70%), **22** (5 mg, 4%), and **23** (50 mg, 19%). **22:** NMR (CCl_4) δ 5.97 (s, 2 H, vinyl), 4.55 (s, 1 H, methine), 2.90-2.65 (m, 2 H), and 2.50-0.65 (m, 9 H). **23:** mp 74.0-74.5 °C; IR (KBr) 3050, 2975, 2930, 2880, 1600, 1555, 1350, 1190, 1180, 1160, 870, and 670 cm^{-1}; NMR (CCl_4) δ 7.66 and 7.22 (2 d, A_2B_2, 4 H, J = 8.0 Hz, aromatic), 5.86 (s, 2 H, vinyl), 4.38 (s, 1 H, methine), 2.72 (s, 2 H), and 2.55-0.75 (m, 9 H). Anal. Calcd for $C_{16}H_{18}O_3S$: C, 66.18; H, 6.25. Found: C, 66.09; H, 6.23.

The NMR spectrum of **19** from acetolysis of the deuterium labeled tosylate (**8-6-*d***) showed that the proton intensity at δ 2.90-2.70 (2 H) was reduced to 1 H indicating that the deuterium stayed on C_1 (or C_6).

Preparative Acetolysis of 9. A solution of **9** (71 mg) in 8.1 mL of acetate buffer in a sealed tube was heated at 25 °C for 42 h. The similar workup procedure gave a mixture of **20** (9 mg, 20%) and **24** (47 mg, 66%). **20:** IR (film) 2960, 2880, 1740 (>C=O), 1364, 1245, 1184, 1175, 1056, 1040, 855, and 670 cm^{-1}; NMR (CCl_4) δ 4.75 (s, 1 H, methine) and 2.65-0.70 (m, 15 H). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 73.35; H, 8.96. **24:** mp 74.5-75.5 °C; IR (KBr) 2990, 2960, 2890, 1600, 1350, 1320, 1190, 1180, 1095, 990, 870, 820, and 670 cm^{-1}; NMR (CCl_4) δ 7.82 and 7.30 (2 d, A_2B_2, 4 H, J = 8.0 Hz, aromatic), 4.62 (s, 1 H, methine), 2.46 (s, 3 H, CH_3-), and 2.40-0.80 (m, 12 H). Anal. Calcd for $C_{16}H_{20}O_3S$: C, 66.18; H, 6.89. Found: C, 65.78; H, 6.96.

Preparative Acetolysis of 10. A solution of **10** (140 mg) in 20 mL of acetate buffer in a sealed tube was heated at 25 °C for 6 h. The similar workup procedure, as mentioned above, yielded 85 mg (99%) of **25:** IR (film) 3040, 2970, 1740 (>C=O), 1370, 1240, 1040, 790, and 740 cm^{-1}; NMR (CCl_4) δ 6.18 (m, 4 H, vinyl), 4.55 (s, 1 H, methine), 3.03-2.57 (m, 6 H), and 1.94 (s, 3 H, CH_3-). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.02; H, 6.99.

Preparative Acetolysis of 11. A solution of **11** (50 mg) in 5 mL of acetate buffer in a sealed tube was heated at 100 °C for 2 h. The similar workup procedure, as mentioned above, gave 37 mg of the products which consist of **25** (55%), **31** (20%), and two unidentified acetates (10 and 6%) by GLC analysis.

Hydrogenations of 19, 21, 22, and 23. A typical run was carried out as follows. A solution of **21** (34 mg, 0.19 mmol) in 10 mL of ethyl acetate containing 7 mg of 5% palladium on carbon was stirred under hydrogen at atmospheric pressure for 2 h. After removal of the catalyst by filtration, the solvent was removed under reduced pressure to give **20** quantitatively. Acetates **19** and **22** also led to **20**, and tosylate **23** led to **24** by hydrogenations.

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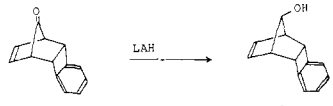

A B

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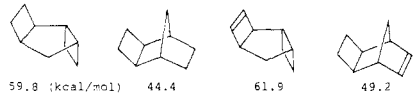

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