The Nature of the Carbonium Ion.
# IX.   The 2-Oxa-6-norbornyl Cation[1]

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Abstract: *exo*-2-Oxabicyclo[2.2.1]heptan-6-ol (**7**) was prepared by the base-catalyzed cyclization of 3,4-epoxycyclo-pentylmethanol (**6**).   The epimeric endo alcohol **9** was obtained from **7** by an oxidation–reduction sequence.   Acetolyses of the arenesulfonate esters of **7** and **9** were effected in buffered solutions.   The major product in all cases was the *exo*-acetate **10b**.   The *endo*-acetate **11b** was also noted in minor amounts.   No elimination products were detected.   Acetolysis of deuterium-labeled *endo*-*p*-bromobenzenesulfonate **12b** revealed that, in formation of the *exo*-acetate, C_6 and C_1 of the cation(s) are equivalent with respect to attack by the nucleophile.   Rate measurements demonstrated the extreme differences in reactivity between the *exo*- and *endo*-arenesulfonates.   Comparisons with the relative rates of the carbocyclic norbornyl analogs, as well as those of other β-alkoxy arenesulfonates, serve as bases for mechanistic interpretation.

In the area of neighboring group participation, perhaps no example has been more heavily studied than that observed in the unimolecular dissociations of 2-norbornyl derivatives.[2]   Of prime interest has been the rationale for the large difference in solvolysis rates between the exo and endo epimers and the great predominance of exo products in most cases.   The involvement of the C_6–C_1 σ bond in ionization and in product determination has been the subject of considerable dispute.[3]   For most heterolytic dissociation reactions of secondary 2-norbornyl derivatives, it is uncertain whether the C_6–C_1 bond is directly involved in ionization (giving the delocalized ion **1**) or only in a subsequent rapid Wagner–Meerwein shift (converting the localized ion **2a** to **2b**).
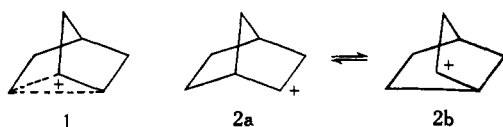
In order to explore this question, several workers[2,4] have employed analogs of the parent compounds where substituents have been added which would be expected to change the steric environment and/or electronic character of the C_6–C_1 bond.   Unfortunately, those studies which utilized derivatives with electron-donating substituents at C_6 (and by consequence could be expected to be quite informative in this question) yielded rather indistinct results.   We decided, therefore, to pursue an alternate course and study the effects of reduced electron-donating ability at the 6 position through replacement of C_6 by an oxygen atom.   The assumption was that, at least inductively, the oxygen would exert an adverse effect on ionizations at C_2.   The magnitude of this effect should reflect the necessity for participation by this bond (or by the oxygen atom directly) in assisting ionization.   Furthermore, the

nature of the products should add some insight with regard to the role of steric features inherent in the basic skeleton.

Some evidence for these suppositions was already present in the investigation by Martin and Bartlett[5] of the solvolyses of *exo*- (**3**) and *endo*- (**4**) 2-chloro-1,-4-endoxycyclohexane.   In these 7-oxa-2-norbornyl derivatives the oxygen, inappropriately positioned for direct assistance to ionization at C_2 *via* an oxonium ion, exerted only a strong rate retarding inductive effect.   The formation of the unstable product, **5**,
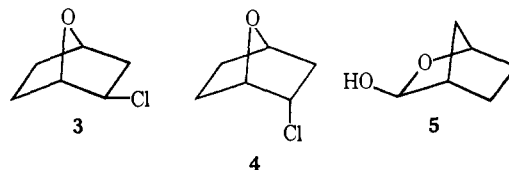
was nevertheless governed by the ultimate stabilization of the positive charge at the original C_1 by the adjacent oxygen.   Since the geometries of the desired 2-oxa-6-norbornyl derivatives were anticipated to vary only slightly from those of **3** and **4**, we felt that useful analogies could be drawn from these solvolyses in interpreting our own results.   We therefore synthesized the *exo*- (**7**) and *endo*- (**9**) 2-oxabicyclo[2.2.1]-heptan-6-ols in preparation for studying the solvolytic behavior of their arylsulfonate esters.

Results

Peracid oxidation of Δ^3-cyclopentenylmethanol[6] afforded a mixture of 3,4-epoxycyclopentylmethanol (**6**) isomers in an approximate 40:60 cis/trans ratio.   This mixture was subjected to base-catalyzed ring closure affording **7** as the only characterizable[7] product in 23% yield.   Chromic oxide oxidation of the bicyclic alcohol **7** gave 2-oxabicyclo[2.2.1]heptan-6-one (**8**).   The ketone, a light-sensitive oil, was reduced with lithium aluminum hydride to give a 12:88 mixture of **7** and the endo alcohol **9** respectively.   Both alcohols

(1) Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Abstract ORGN 108.

(2) For a comprehensive survey of the initial work in this area, see J. A. Berson in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, Chapter 3.

(3) See S. Winstein, *J. Amer. Chem. Soc.*, **87**, 381 (1965), and references cited therein.

(4) For example, P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, **87**, 375 (1965); S. Winstein, *et al.*, *ibid.*, **87**, 378 (1965); P. G. Gassman and J. M. Hornback, *ibid.*, **91**, 4282 (1969).

(5) J. C. Martin and P. D. Bartlett, *ibid.*, **79**, 2533 (1957).

(6) (a) G. H. Schmid and A. W. Wolkoff, *J. Org. Chem.*, **32**, 254 (1967); (b) J. Meinwald, P. G. Gassman, and J. K. Crandall, *ibid.*, **27**, 3366 (1962).

(7) The uncyclizable cis isomer conveniently polymerized during the course of the reaction.

7 and **9** were converted by standard techniques (see Experimental Section) to their p-bromobenzenesulfonate (**10a** and **11a**) and acetate (**10b** and **11b**) esters. The exo alcohol **7** was additionally converted to its p-toluenesulfonate (**10c**) and p-nitrobenzoate (**10d**) esters. For deuterium-labeling studies, endo-2-oxabicyclo[2.2.1]hept-6-yl-6-d p-bromobenzenesulfonate (**12b**) was prepared from ketone **8** via lithium aluminum deuteride reduction, and the subsequent esterification of alcohol **12a** by a procedure analogous to that used in synthesis of **11a**. Structures of all alcohols, esters, and the ketone were substantiated by infrared, nmr, and elemental analyses.

10a, R = Bs
  b, R = Ac
  c, R = Ts
  d, R = PNB

12a, R = H
  b, R = Bs

11a, R = Bs
  b, R = Ac
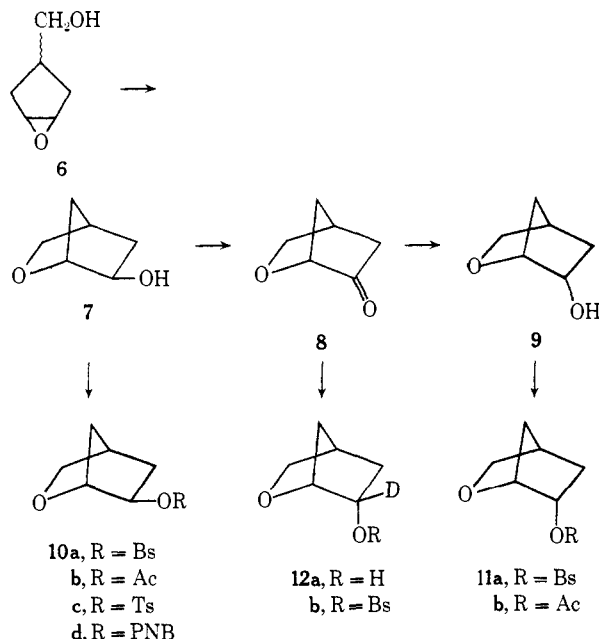
Acetolyses of the p-bromobenzenesulfonate esters **10a**, **11a**, and **12b**, and the p-toluenesulfonate ester **10c**, were conducted in 0.15 M solutions which were 0.2 N in potassium acetate buffer. In product studies, runs were analyzed after approximately seven half-lives. The product mixtures from the exo esters **10a** and **10c** consisted almost entirely of exo-acetate **10b**. Careful gc analysis revealed the additional presence of the endo epimer **11b** in a maximum relative proportion of 0.4%. No elimination product(s) could be detected. The endo-p-bromobenzenesulfonates **11a** and **12b** also afforded mainly **10b**, but in this case the exo ester comprised only 85% of the recovered product. endo-Acetate **11b** was detected as 2% of the product mixture, and the remaining 13% consisted of at least four unidentified[8] acetates. Again, no elimination products (or their decomposition by-products) could be verified. Control experiments with acetates **10b** and **11b** (conducted by heating each pure acetate in the buffered acetolysis medium at 149° for seven half-lives of **11b**) showed both to be stable to the reaction conditions, thereby indicating the product mixtures to be solely the results of the primary reaction. Nmr analysis of the acetate mixture from the deuterium-labeled ester

(8) Ir, gc, and mass spectral analyses of these products revealed them to be acetates and diacetates. Of nine conceivable products resulting from elimination reactions of the original esters, or from fragmentation processes, all could be ruled out by spectral analyses. The homogeneities of **11a** and **12b** were likewise reconfirmed by careful chromatographic analyses.

12b showed the exo-acetate to be, within limits of the measuring technique, an equal mixture of 1-d and 6-d isomers.

As it was apparent from the product studies that there existed a considerable difference in reactivity between the exo- and endo-arylsulfonate esters, the rate measurements of **10a** and **10c** were conducted at 25–45°, while those of **11a** and **12b** were performed at 149–189°. The reactions were followed by standard titrimetric methods, and graphs (log [ROTs] vs. t) of the data showed linear first-order behavior to a minimum of 87% reaction. Table I summarizes the results. Rates given are the averages of at least two runs.

Table I. Rate Data for Potassium Acetate Buffered Acetolyses of 2-Oxabicyclo[2.2.1]hept-6-yl Arenesulfonates

Ester	T, °C	$k \times 10^5$, sec^{-1}	$t_{1/2}$, hr	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
10a	25.0	21.8	0.92		
10c	25.0	3.8	5.13	23.4	−0.3
	45.0	45.0	0.43		
11a	25.0	$2.9 \times 10^{-7\ a}$	$6.5 \times 10^{7\ a}$		
	149.0	1.2	15.5	30.5	−9.4
	170.0	9.3	2.16		
	189.5	30.0	0.65		
12b	149.0	1.2	15.4		

^{a} Extrapolated from data at higher temperatures.

Discussion

Two observations immediately differentiate the acetolyses of the 2-oxa-6-norbornyl derivatives from those of their 2-norbornyl and 7-oxa-2-norbornyl (**3, 4**) counterparts. First, the enormous exo/endo rate ratio of the 2-oxa-6-norbornyl p-bromobenzenesulfonates (**10a/11a** = 7 × 10⁷ at 25°) dwarfs the approximately 300-fold rate difference observed[2,5] for the other systems at the same temperature (see Table II). Second, the detection of measurable

Table II. Comparisons of Solvolytic Rates for Norbornyl and Oxanorbornyl p-Bromobenzenesulfonates at 25°
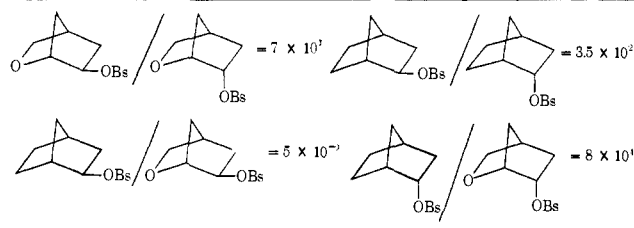
amounts of endo-acetate **11b** in the product mixtures from both **10a** and **11a** is unlike the essentially homogeneous exo-acetate obtained from the carbocyclic 2-norbornyl esters. An additional peculiarity of the **10a/11a** rate ratio is its lack of similarity even to that observed for acetolyses of the 9-oxabicyclo[4.2.1]non-2-yl p-bromobenzenesulfonates (**13** and **14**).[9] In this latter case, despite superficial resemblances to **10a** and **11a** in geometries of leaving group and ether oxygen, the **13/14** rate ratio was only 10.

(9) L. A. Paquette and P. C. Storm, J. Amer. Chem. Soc., **92**, 4295 (1970).

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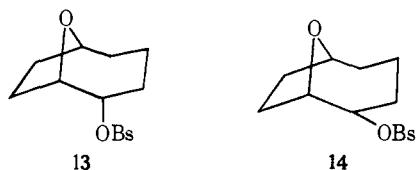
One may conclude from these observations that the oxygen of the 2-oxa-6-norbornyl system is particularly well situated to interact with properly oriented orbitals at C_6. Further support for this comes from the n → π* absorption of ketone **8** (λ_{max}^{EtOH} 300 nm (ϵ 33)) which shows a clear bathochromic shift from that of its carbocyclic counterpart (λ_{max}^{EtOH} 288 nm (ϵ 27)). All of this implies that one may anticipate rate-accelerating participation by oxygen for ionizations of appropriately positioned substituents at C_6. To estimate the magnitude of this effect, the extent of the rate decelerating inductive effect by the β oxygen must be established. Careful consideration of various solvolytic reactions undergone by β-alkoxy derivatives led us to adopt the inductive rate-retarding factor of 2000 observed for solvolysis of **3**.[5,10] The correctness of this choice was interestingly amplified by its application in the Foote–Schleyer method for estimation of nonassisted solvolysis rates.[11] Utilizing appropriate bond angle, torsional, and nonbonded interaction strain values,[12] the rate of acetolysis of 2-oxabicyclo[2.2.1]hept-6-yl p-toluenesulfonate at 25°, predicted by these calculations, was 2.69×10^{-12} sec^{-1}. Allowing a fivefold rate difference for the conversion of p-toluenesulfonate to p-bromobenzenesulfonate rates,[13] the predicted value corresponds quite closely to the rate observed for the endo ester **11a** (2.9×10^{-12} sec^{-1}), and consequently diverges drastically from the rate of the exo ester **10a**. The difference between calculated and measured rate values is considered by Schleyer[11] to be a measure of the anchimeric assistance. In this case log (anchimeric assistance) = 8.7 for the rapidly solvolyzing **10a**. This places the exo ester very high on the anchimeric assistance scale, exceeding exo-2-norbornyl p-toluenesulfonate by five orders of magnitude and being surpassed only by a few anti-7-norbornenyl and anti-7-benznorbornenyl arylsulfonates.[11] These observations notwithstanding, one fact is quite obvious from a simple comparison of rates: the only twofold rate difference between the exo carbocyclic ester and **10a** implies that the degree of assistance and the β-oxygen inductive effect are nearly of equal counteracting magnitudes in **10a**. By contrast, the large difference between the rates of the endo epimers of these esters demonstrates an extreme hindrance to ionization by the oxygen in **11a**. This may most likely be attributed to the adverse inductive effect in concert with the increased ring strain in the oxanorbornyl skeleton[14] and the repulsive interaction of the nonbonded electrons on oxygen with the developing negative charge on the leaving group. The assumption

must be that the geometry of the ring system allows the oxygen to offer no assistance in ionization of **11a**. On the basis of this evidence one is led to the conclusion that the transition state for ionization of **11a** must possess a cationic portion resembling **15**, while that of **10a** must have the oxonium structure **16**.

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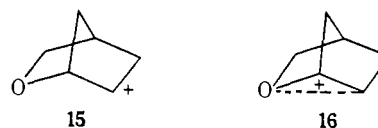
The deuterium-labeling experiments support a symmetrical species as the major product determining ion from **12b** (hence, **11a**). In all probability the same is true for **10a**. A simplifying assumption is that this species resembles **16** for both exo and endo epimers. This explains the great preference for formation of exo-acetate **10b** and the apparent equivalence of C_6 and C_1 with respect to attack by the nucleophile. The identification of endo-acetate **11b** as an additional product, however, complicates the mechanistic description. In the cases of the endo-p-bromobenzenesulfonate **11a**, one may rationalize the slight retention of configuration by postulating an attack by the nucleophile on the endo face of cation **15** prior to its transformation to **16**. (The conversion **15** → **16** may be somewhat retarded by hydrogen bonding between solvent and the β oxygen). For the exo-sulfonate **10a** two main possibilities exist: (1) "leakage" from the oxonium ion **16** to the localized species **15**, followed by attack on the latter species; and (2) a transfer of hydrogen bonded solvent from the β oxygen to C_6 in **16** by a cyclic process (see **17**). The extremely

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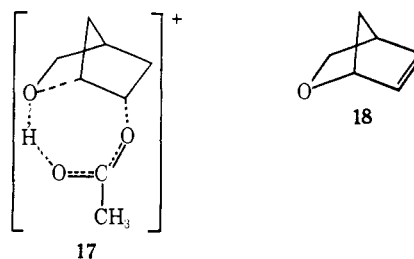
small amount of endo product formed precludes experimental verification of either possibility. In light of our previous studies[15] of the norbornyl cation under conditions where the delocalized ion → localized ion conversion should have been detected (if it existed) and considering the unfavorable energetics probable for the loss of oxygen stabilization, it seems that the cyclic process may be favored for the minor product.

The failure to detect any elimination products is interesting but explicable if one remembers that the main elimination mode for the carbocyclic series leads to nortricyclene rather than norbornylene.[3] As the pathway to a tricyclic oxa counterpart of nortricyclene does not exist in this case, only the olefin **18** might be anticipated. The failure to detect **18** suggests that elimination is either too minor a process to consider or that **18** itself reacts rapidly enough with the solvent, affording **10b**, such that it is impossible to detect. Based on analogy to the norbornyl solvolyses, the latter possibility should make an extremely small contribution to the mechanistic scheme.

(10) The geometrical relationships of the oxygen and leaving group in the 7-oxa-2-norbornyl derivatives seem more similar to those in our system than in most others reported.

(11) P. v. R. Schleyer, J. Amer. Chem. Soc., 86, 1854 (1964).

(12) ν_{CO} 1769 cm^{-1}; $\phi_{ij} = 0$, 30°; ground state − torsional strain (GS-TS) (10a) = 0.3 kcal; GS-TS (11a) = 1.3 kcal.

(13) This is the rate ratio observed for 10a and 10c.

(14) The greater ring strain in the oxa analog is most clearly seen in the carbonyl infrared stretching frequencies of 8 (ν_{max} 1769 cm^{-1}) and norcamphor (ν_{max} 1751 cm^{-1}).

(15) L. A. Spurlock and T. E. Parks, J. Amer. Chem. Soc., 92, 1279 (1970).

Experimental Section[16]

4-Hydroxymethylcyclopentene was prepared through the lithium aluminum hydride reduction of 3-cyclopentene-1-carboxylic acid[6a] by the method of Meinwald, Gassman, and Crandall[6b] in yield of 85%, bp 90–91° (41 mm), $n^{23.5}$D 1.4709 [lit.[6b] bp 98–99° (57 mm), n^{22}D 1.4670].

3,4-Epoxycyclopentylmethanol (6). To 74.3 g (0.366 mol) of 85% *m*-chloroperbenzoic acid dissolved in 700 ml of chloroform was added dropwise 35.8 g (0.366 mol) of 4-hydroxymethylcyclopentene.[17] The temperature was kept below 25° during the addition. After complete addition, the mixture was allowed to stir at room temperature overnight. The excess oxidizing agent was then destroyed with 10% sodium sulfite and the resulting mixture basified with saturated sodium bicarbonate solution. The reaction mixture was continuously extracted with ethyl ether for 36 hr. The ether extract was dried and concentrated affording 39.0 g (93.3%) of a mixture of cis and trans epoxides in an approximately 40:60 proportion. An analytical sample was prepared by distillation: bp 78–81° (2.2 mm); ir (neat) 3425, 3040, 2940, 2875, 1440, 1390, 1300, 1230, 1100, 1035, 965, 944, and 840 cm⁻¹; nmr (CCl₄) τ 6.11 (s), 6.61 (m), 7.43–9.00 (m).

Anal. Calcd for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found: C, 63.40; H, 8.56.

exo-**2-Oxabicyclo[2.2.1]heptan-6-ol (7).** To 2 l. of *tert*-butyl alcohol, freshly distilled from sodium, was added 25.7 g (0.66 g-atom) of potassium metal, and the mixture was stirred at reflux under a nitrogen atmosphere until all potassium had dissolved. To this solution was added 39.0 g (0.342 mol) of crude **6**. The mixture was allowed to stir for 48 hr at reflux. The cooled solution was then acidified to pH 7, the salts were removed by filtration, and the filtrate was concentrated by carefully distilling off the excess *tert*-butyl alcohol. The residue was titurated with ethyl ether and the resulting ether solution treated with activated charcoal for 18 hr at room temperature. This was then filtered, dried, and concentrated, affording 30.5 g of crude **7**. This liquid was treated with acetyl chloride in pyridine (see subsequent procedure) to form the acetate derivative **10b** in 29.5% yield. To 1.50 g (39.5 mmol) of lithium aluminum hydride in ethyl ether was added 12.3 g (79.0 mmol) of acetate **10b** with stirring. The reaction mixture was heated at reflux overnight and then treated with base in a conventional work-up to afford 8.4 g (93.3%) of pure *exo*-2-oxabicyclo[2.2.1]heptan-6-ol (**7**).[18] Preparative gc afforded an analytical sample as a white waxy solid: mp 86–94°; ir (CCl₄) 3425, 2990, 2870, 1460, 1440, 1330, 1085, 1060, 1005, 955, 920, and 885 cm⁻¹; nmr (CCl₄) τ 5.83 (1 H, s), 6.09 (1 H, br s), 6.25 (1 H, d sext), 6.50 (1 H, d tr), 6.80 (1 H, d), 7.57 (1 H, br s), 7.95–9.00 (4 H, m); mass spectrum (70 eV) *m/e* (rel intensity) 114 (35.8), 96 (17.3), 71 (22.2), 70 (43.8), 69 (100.0), 68 (21.6), 57 (16.7), 55 (33.9), 44 (63.0), 43 (51.9), 42 (31.5), 41 (53.8), 39 (24.1).

exo-**2-Oxabicyclo[2.2.1]hept-6-yl Acetate (10b).** To 30.5 g (0.268 mol) of crude **7** in 70 ml of pyridine being stirred at 0° was added dropwise 21.0 g (0.268 mol) of acetyl chloride. After complete addition the mixture was allowed to stand at 5° overnight. The mixture was poured into 200 ml of ice–water and extracted four times with 50 ml of ethyl ether. The combined extracts were washed with a minimum amount of cold 10% hydrochloric acid[19] and once with 50 ml of saturated sodium bicarbonate solution, dried, and concentrated and the resulting residue distilled at 48° (0.1 mm), $n^{24.5}$D 1.4546, to give 12.3 g (29.5%) of *exo*-2-oxabicyclo-

[2.2.1]hept-6-yl acetate (**10b**): ir (film) 3000, 2950, 2890, 1730, 1360, 1240, 1080, 1060, 1020, 955, and 880 cm⁻¹; nmr (CCl₄) τ 5.36 (1 H, d sext), 5.86 (1 H, br s), 6.43 (1 H, d tr), 6.69 (1 H, d), 7.49 (1 H, br s), 8.03 (3 H, s), 7.82–9.21 (4 H, m); mass spectrum (70 eV) *m/e* (rel intensity) 156 (0.7), 113 (16.7), 96 (52.0), 81 (16.7), 69 (100.0), 67 (15.6), 44 (23.3), 43 (94.1) 41 (20.7), 40 (25.3).

Anal. Calcd for $C_8H_{12}O_3$: C, 61.52; H, 7.74. Found: C, 60.97; H, 7.62.

exo-**2-Oxabicyclo[2.2.1]hept-6-yl *p*-nitrobenzoate (10d)** was prepared from 1.0 g (8.8 mmol) of **7** and 1.5 g (8.1 mmol) of *p*-nitrobenzoyl chloride in 6 ml of pyridine by a method similar to that for acetate **10b**. Work-up and crystallization from ether–pentane afforded 0.6 g (28.3%) of a cream colored crystalline solid: mp 96.5–97.0°; ir (mull) 1720, 1610, 1380, 1345, 1310, 1280, 1210, 1060, 1020, 965, 885, 875, 855, and 720 cm⁻¹; nmr (CDCl₃) τ 1.62 (4 H, s), 4.92 (1 H, d sext), 5.54 (1 H, br s), 6.27 (1 H, d tr), 6.53 (1 H, d), 7.32 (1 H, br s), 7.52–8.83 (4 H, m).

Anal. Calcd for $C_{13}H_{13}NO_5$: C, 59.13; H, 4.98; N, 5.32. Found: C, 59.43; H, 4.78; N, 5.147.

exo-**2-Oxabicyclo[2.2.1]hept-6-yl *p*-toluenesulfonate (10c)** was prepared from 1.6 g (14 mmol) of **7** and 2.9 g (15.2 mmol) of *p*-toluenesulfonyl chloride in 15 ml of pyridine by a method similar to that used for **10b**. The work-up afforded 2.9 g (77%) of light tan solid. An analytical sample was obtained by ether–pentane recrystallization of a small portion of crude *p*-toluenesulfonate **10c**: mp 61–62°; ir (melt) 2990, 2950, 2880, 1600, 1360, 1180, 1170, 1090, 1050, 970, 950, 920, 875, 810, and 665 cm⁻¹; nmr (CDCl₃) τ 2.39 (4 H, A₂B₂), 5.53 (1 H, d sext), 5.79 (1 H, br s), 6.43 (1 H, d tr), 6.73 (1 H, d), 7.48 (1 H, partially hidden br s), 7.57 (3 H, s), 8.00–8.87 (4 H, m).

Anal. Calcd for $C_{13}H_{16}O_4S$: C, 58.19; H, 6.01; S, 11.95. Found: C, 57.95; H, 6.14; S, 11.95.

exo-**2-Oxabicyclo[2.2.1]hept-6-yl *p*-Bromobenzenesulfonate (10a).** The *exo-p*-bromobenzenesulfonate was prepared from 8.4 g (73.7 mmol) of **7** and 19.2 g (75.0 mmol) of *p*-bromobenzenesulfonyl chloride in 40 ml of pyridine by the method previously described for **10b** affording 4.0 g (16.2%) of white crystalline solid, mp 54–57°.[20] An analytical sample was obtained by recrystallizing a small portion of solid in ether–pentane: mp 61–62°; ir (mull) 1580, 1190, 1170, 1100, 1075, 1060, 1015, 960, 930, 880, 825, and 740; nmr (CCl₄) τ 2.41 (4 H, s), 5.67 (1 H, d sext), 5.92 (1 H, br s), 6.57 (1 H, d tr), 6.85 (1 H, d), 7.53 (1 H, br s), 7.83–8.93 (4 H, m).

Anal. Calcd for $C_{12}H_{13}BrO_4S$: C, 43.25; H, 3.93; Br, 23.98; S, 9.62. Found: C, 43.71; H, 3.89; Br, 24.04; S, 9.48.

2-Oxabicyclo[2.2.1]heptan-6-one (8). To a solution containing 50.0 g (0.194 mol) of dipyridinechromium(VI) oxide[21] in 125 ml of methylene chloride was added at ambient temperature 4.0 g (0.035 mol) of **7**. The mixture was allowed to stand for 15 min and then filtered through Filter-cel. The orange filtrate was dried and concentrated to give the crude ketone. This residue was distilled at 62–62.5° (5 mm) to afford 2.1 g (53.5%) of ketone **8**:[22] n^{26}D 1.4571; ir (film) 2970, 2900, 1769, 1160, 1020, 965, 935, and 860 cm⁻¹; nmr (CCl₄) τ 6.02 (1 H, d), 6.18 (1 H, d tr), 6.42 (1 H, d), 7.15 (1 H, br m), 8.08 (4 H, m); uv, λ_{max}^{EtOH} 300 nm (ε 33).

Anal. Calcd for $C_6H_8O_2$: C, 64.27; H, 7.19. Found: C, 64.17; H, 7.07.

endo-**2-Oxabicyclo[2.2.1]heptan-6-ol (9).** To 0.80 g (21.1 mmol) of lithium aluminum hydride being stirred in 50 ml of ethyl ether was added dropwise 2.00 g (17.9 mmol) of **8** dissolved in 10 ml of ethyl ether. The mixture was stirred at reflux for 18 hr and then treated with base in a conventional work-up to afford 2.0 g (98%) of crude material. The crude alcohol was gc analyzed and found to contain endo (88%) and exo (12%) alcohols. Preparative gc afforded an analytical sample of **9** as a white waxy solid: mp 110–112°; ir (mull) 3400, 1160, 1140, 1115, 1080, 1030, 995, 915, 870, 835, and 755 cm⁻¹; nmr (CDCl₃) τ 5.60 (1 H, br s), 5.69 (1 H, partially hidden d tr), 6.17 (1 H, d tr), 6.34 (1 H, d), 7.19 (1 H, br s), 7.51 (1 H, br s), 7.67–9.18 (4 H, m); mass spectrum (70 eV) *m/e* (rel intensity) 114 (15.8), 71 (15.9), 70 (38.9), 69 (100.0), 68 (20.4), 57 (17.5), 55 (28.4), 44 (59.7), 43 (36.1), 42 (30.8), 41 (52.7), 39 (27.1).

(16) Infrared spectra were determined with a Perkin-Elmer Infracord using sodium chloride optics. The nmr determinations were carried out on a Varian Associates A-60A spectrometer; approximately 20% solutions in CCl₄ or CDCl₃ were employed with tetramethylsilane as the internal standard. A Perkin-Elmer F-11 gas chromatograph (12 ft × ¹/₈ in., 15% LAC 728 on Chromosorb W), a F&M Model 500 gas chromatograph (12 ft × 0.25 in., 15% LAC 728 on Chromosorb W) and an Aerograph Model A-90-P gas chromatograph (6 ft × ³/₈ in., 30% LAC 728 on Chromosorb W) were utilized in product studies. The mass spectra were carried out on a Hitachi Perkin-Elmer RMU-6D mass spectrometer. The ultraviolet spectra were determined on a Cary Model 14 recording spectrophotometer. Elemental analyses were performed by Micro-Analysis, Inc., of Wilmington, Del.

(17) Ethyl ether, benzene, and methanol were also used as solvents; however, it was found that chloroform and methylene chloride gave the highest yield of product.

(18) A less efficient purification procedure for **7** involved flash distillation at 80° (0.1 mm) of the original crude reaction mixture.

(19) Only enough cold acid was used to render the water layer just acidic. Over-acidification will destroy most of the exo derivatives of this ring system.

(20) The extreme reactivity of this *p*-bromobenzenesulfonate was such that it became necessary to store it at Dry Ice temperature.

(21) For preparation of dipyridinechromium(VI) oxide, see J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, **30**, 3363 (1968).

(22) For a more recent modification of dipyridinechromium(VI) oxide as an oxidizing agent, see R. Ratcliffe and R. Rodehorst, *J. Org. Chem.*, **35**, 4000 (1970).

endo-2-Oxabicyclo[2.2.1]hept-6-yl *p*-Bromobenzenesulfonate (11a). To 4.09 g (16.0 mmol) of *p*-bromobenzenesulfonyl chloride in 20 ml of pyridine being stirred at 5° was added 1.73 g (15.2 mmol) of crude 9.[23] After addition the mixture was allowed to stand at 5° overnight. The reaction mixture was poured into ice–water and extracted several times with ethyl ether. The combined extracts were washed with 10% hydrochloric acid[24] and saturated sodium bicarbonate, dried, and concentrated and the resulting crude solid recrystallized from chloroform–pentane to give 1.74 g (39.6%) of *endo*-2-oxabicyclo[2.2.1]hep-6-yl *p*-bromobenzenesulfonate (11a): mp 128.5–129°; ir (mull) 1570, 1320, 1300, 1280, 1240, 1190, 1180, 1100, 1070, 1015, 990, 965, 940, 925, 895, 880, 845, 840, 830, 820, 775, and 740 cm^{-1}; nmr (CDCl$_3$) τ 2.38 (4 H, A$_2$B$_2$), 5.25 (1 H, d tr), 5.84 (1 H, tr), 6.27 (1 H, d tr), 6.44 (1 H, d), 7.55 (1 H, br s), 7.83–8.83 (4 H, m).

Anal. Calcd for C$_{12}$H$_{12}$BrO$_4$S: C, 43.25; H, 3.93; S, 9.62. Found: C, 43.10; H, 3.87; S, 9.59.

endo-2-Oxabicyclo[2.2.1]hept-6-yl acetate (11b) was prepared from 166 mg (1.46 mmol) of crude 9[23] and 178 mg (1.50 mmol) of acetyl chloride in 1 ml of pyridine by a method similar to that utilized for acetate 10b. Work-up afforded 112 mg (49%) of both *endo*- and *exo*-acetates. The mixture was gc analyzed and found to contain *endo*- (73.8%) and *exo*- (26.2%) acetates. Preparative gc provided an analytical sample of 11b as a colorless, sweet-smelling liquid: ir (film) 2990, 2950, 2885, 1730, 1440, 1380, 1300, 1260, 1175, 1125, 1100, 1080, 1045, 1010, 975, 930, 905, 880, and 840 cm^{-1}; nmr (CCl$_4$) τ 5.27 (1 H, d tr), 5.75 (1 H, tr), 6.30 (1 H, d tr), 6.51 (1 H, d), 7.56 (1 H, br s), 8.01 (3 H, s), 7.75–9.00 (4 H, m); mass spectrum (70 eV) m/e (rel intensity) 156 (0.9), 113 (14.4), 96 (51.1), 81 (21.0), 69 (100.0), 43 (93.7), 41 (20.9).

endo-2-Oxabicyclo[2.2.1]heptan-6-ol-6-*d* (12a). To 0.84 g (20.0 mmol) of lithium aluminum deuteride being stirred in 140 ml of ethyl ether was added dropwise 4.18 g (37.4 mmol) of ketone 8 dissolved in 10 ml of ethyl ether. The mixture was stirred at reflux for 5 hr and then treated with base in a normal work-up to afford 3.23 g (75%) of a mixture of endo and exo alcohols[23] as a white waxy solid: ir (film) 3440, 2990, 2890, 1460, 1340, 1300, 1200, 1100, 1070, 980, 960, 935, 920, 880, 840, 805, and 760 cm^{-1}.

endo-2-Oxabicyclo[2.2.1]hept-6-yl-6-*d* *p*-Bromobenzenesulfonate (12b). The *p*-bromobenzenesulfonate was prepared from 3.23 g (28.1 mmol) of crude 12a[23] and 7.50 g (29.4 mmol) of *p*-bromobenzenesulfonyl chloride in 40 ml of pyridine by the method previously described for 11a, affording 7.70 g (93%) of crude 12b. Recrystallization from chloroform–pentane gave 4.98 g (60.4%) of pure 12b:[25] mp 127–127.5°; ir (mull) 1575, 1200, 1180, 1100, 1070, 1040, 1015, 975, 965, 950, 945, 930, 880, 870, 820, 770, and 740 cm^{-1}; nmr (CDCl$_3$) τ 2.26 (4 H, A$_2$B$_2$), 5.79 (1 H, d), 6.22 (1 H, d tr), 6.37 (1 H, d), 7.53 (1 H, br s), 7.66–8.84 (4 H, m).

Anal. Calcd for C$_{12}$H$_{12}$BrO$_4$SD: C, 43.12; H, 3.62; D, 0.60; S, 9.59. Found: C, 43.31; H, 3.95; S, 9.43.

Product Studies. Acetolysis of 10a. To 0.734 g (2.22 mmol) of 10a in a glass tube was added 11 ml of 0.206 *N* potassium acetate in acetic acid containing 1% acetic anhydride. The tube was flushed with nitrogen, sealed, and heated at 150° for 10.5 hr. The solution was then cooled, diluted with 100 ml of ice water, and extracted with four 50-ml portions of ethyl ether. The combined extracts were washed with 25-ml aliquots of saturated sodium bi-

carbonate solution until neutral, dried, and concentrated to give 0.355 g (103%) of a mixture of acetates 10b and 11b.[26]

To 0.760 g (2.00 mmol) of lithium aluminum hydride in ethyl ether was added 0.200 g (1.28 mmol) of the acetate mixture. The reaction mixture was stirred for 4 hr and then treated with base in a normal work-up to afford 0.145 g (99%) of alcohol mixture. The reduced mixture was gc analyzed and found to contain 7 (99.64%) and 9 (0.36%).

Product Studies. Acetolysis of 11a. To 0.182 (0.55 mmol) of 11a in a glass tube was added 4.5 ml of 0.206 *N* potassium acetate in acetic acid containing 1% acetic anhydride. The tube was flushed with nitrogen, sealed, and heated at 152° for 115 hr. The solution was worked up in a manner similar to that utilized for 10a, affording 0.129 g (151%) of a mixture of acetates 10b (85.04%), 11b (1.66%), and at least four unknown acetates.[8]

Product Studies. Acetolysis of 10c. To 0.200 g (0.75 mmol) of 10c in a glass tube was added 2.4 ml of 0.206 *N* potassium acetate in acetic acid containing 1% acetic anhydride. The tube was flushed, sealed, heated, and worked up similarly to 10a, affording 0.100 g (96%) of a mixture of acetates 10b (>99%) and 11b (<1%).[26]

Product Studies. Acetolysis of 12b. To 0.212 g (0.635 mmol) of 12b in a glass tube was added 4.5 ml of 0.206 *N* potassium acetate in acetic acid containing 1% acetic anhydride. The tube was flushed with nitrogen, sealed, and heated at 189.5° for 15 hr. The solution was worked up similarly to 10a affording 0.125 g (125%) of a mixture of acetates. The nmr spectrum of the acetolysis product showed that the mixture contained mainly *exo*-2-oxabicyclo[2.2.1]-hept-6-yl acetate. This contained 0.45 atom of deuterium at C$_1$ and 0.55 atom of deuterium at C$_6$.

Kinetic Studies. J. T. Baker Co. reagent grade analyzed glacial acetic acid, containing 1% by weight of added acetic anhydride, was used for the acetolysis runs, and in the preparation of the standard solutions. Standard perchloric acid in glacial acetic acid was prepared and standardized against potassium acid phthalate. A potassium acetate solution in glacial acetic acid was standardized against standard perchloric acid in glacial acetic acid.

The indicator used was a 0.2% solution of Crystal Violet in glacial acetic acid. The acetolysis kinetics were run following two general procedures.

Procedure A. The *p*-bromobenzenesulfonate was weighed into a volumetric flask and diluted with sufficient standard potassium acetate in glacial acetic acid to afford an approximately 0.15 *M* solution. Aliquots (0.5 ml) of this solution were sealed in Pyrex tubes and submerged in the constant-temperature bath. At appropriate time intervals, tubes were withdrawn and rapidly cooled in ice-water; the contents were poured into 25 ml of glacial acetic acid containing petroleum ether, and the remaining potassium acetate was titrated with standard perchloric acid.

Procedure B. The *exo*-arylsulfonate (10a or 10c) was weighed into a volumetric flask and was diluted with the appropriate amount of standard potassium acetate in glacial acetic acid to give approximately 0.15 *M* solution. The volumetric flask was submerged in the constant-temperature bath. At selected time intervals aliquots (0.5 ml) of this solution were withdrawn with a calibrated pipet and poured immediately into 25 ml of glacial acetic acid containing petroleum ether, and the excess potassium acetate was titrated with standard perchloric acid. Infinity titers in both procedures were taken at approximately eight half-lives. The first-order rate constants were determined from a computer (IBM 360) fitted least-squares plot of ln [ROBs] *vs.* time.

(23) A mixture of endo (88%) and exo (12%) alcohols was indicated by gc analysis.

(24) The material was treated with enough acid to destroy any *exo-p*-bromobenzenesulfonate that had formed in the reaction.

(25) Nmr analysis of 12b showed it to contain >0.95 atom of deuterium at C$_6$.

(26) This was determined by ir, nmr, and gc analyses.