(18) In our experiment the Beckmann rearrangement of 1-oxime under the similar conditions with PPE afforded **2** and **3** in 30:70 ratio at 90% conversion. See also ref 3.
(19) E. M. Engler, L. Chang, and P. v. R. Schleyer, *Tetrahedron Lett.*, 2525 (1972).
(20) A considerable stabilization effect of alkyl group on the transition state has been reported recently in the solvolytic fragmentation of unsymmetrical 4-piperidinol derivatives: C. A. Grob, W. Kunz, and P. R. Marbet, *Tetrahedron Lett.*, 2613 (1975).
(21) Cf. ref 4a and V. G. Keizer, J. G. Korsloot, F. W. v. Deursen and M. E. v. d. Heeden, *Tetrahedron Lett.*, 2059 (1970).
(22) For example, protoadamantane, adamantane, homoadamantane, and 1,1-bishomoadamantane have been reported to have calculated strain energy 18.29, 6.87, 14.59, and 23.46 kcal/mol, respectively: E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8005 (1973).
(23) Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer. Melting points were determined with a Yanagimoto micromelting point apparatus (hot-stage type) in sealed tube and are uncorrected. Ir spectra were taken with a Jasco IRA-1 spectrometer. NMR spectra were taken with a JEOL C-60HL or a JEOL JNM-MH-100 spectrometer using Me_4Si as internal standard, and mass spectra with a JEOL 01SG spectrometer at 75 eV. GLC analyses were performed with a Neva gas chromatograph, Model 1400, and preparative GLC with a Varian Aerograph Model 700.
(24) H. C. Brown and C. P. Garg, *J. Am. Chem. Soc.*, **83**, 2952 (1961).
(25) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, N.Y., 1967, p 892.
(26) See ref 25, p 145.

Solvolysis of Benzobicyclo[3.2.1]octenylmethyl Tosylates

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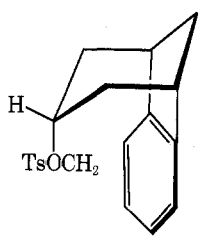
exo- and *endo*-benzobicyclo[3.2.1]octenylmethyl tosylates (**1** and **11**) were synthesized from the pyrrolidine enamine of 2-indanone using methyl-β,β'-dibromoisobutyrate (**3**) in an α,α' annelation reaction. The endo hydroxymethyl tosylate **1** undergoes acetolysis at 75 °C with a rate of 2.3×10^{-5} s^{-1}, 58 times that of the exo methyl tosylate (**11**). The products of the acetolysis of **1** were completely rearranged having a benzobicyclo[3.3.1]nonane skeleton (acetate **13** and olefin **12**).

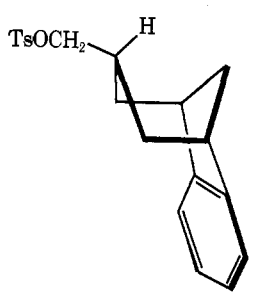
Participation of an aromatic moiety to the site of a developing cation is an area of organic chemistry which continues to be a source of fascinating and informative investigations.[1] Included among those structural factors which affect the contribution of aryl π-participation are the orientation of the aromatic ring with respect to the leaving group, the nature of the substituents on the aromatic ring, and the number and type of bonds in the chain between the aromatic ring and leaving group as well as the number of degrees of freedom in that chain. In spite of many extensive studies, there are few examples of systems in which a remote, developing primary cation is constrained to the face of an aromatic ring.[2] The benzobicyclo[3.2.1]octenyl-*endo*-methyl tosylate structure (**1**) contains this advantageous characteristic.



1

The synthetic design for a molecule such as **1** in which only a single mode of participation was likely to occur and in which the essential configurational and steric relationships were maintained was facilitated by the demonstrated ability of our α,α' annelation reaction[3] to provide unstable endo stereoisomers in the construction of bicyclic frameworks. Annelation of the pyrrolidine enamine of 2-indanone[4] **2** with β,β'-dibromoisobutyrate **3** yielded crystalline benzobicyclo[3.2.1]octenyl ester **5** by way of the intermediate enamine acrylate **4**.[5] The endo stereochemistry of the ester function in bicyclic **5** was supported by its conversion to exo epimer **6** with sodium methoxide–methanol, accompanied by a shift in the ^1H NMR resonance of the ester methyl to lower field. The ester methyl of endo ester **5** lies in the shielding cone of the benzene ring and resonates at 0.5 ppm higher field in the ^1H NMR than the methyl of exo ester **6**. Keto ester **5** was converted to its tosylhydrazone and reduced with lithium aluminum hydride.[6] The resulting endo alcohol **7** was characterized as acetate **8**. Starting from exo ester **6**, an identical route yielded alcohol **9** and acetate **10**. The ^1H NMR data of alcohols **7** and **9** and acetates **8** and **10** indicated that the stereochemistry of esters **5** and **6** was maintained during the transformations. The *p*-toluenesulfonates **1** and **11** were prepared from the corresponding alcohols in the usual manner.[7]

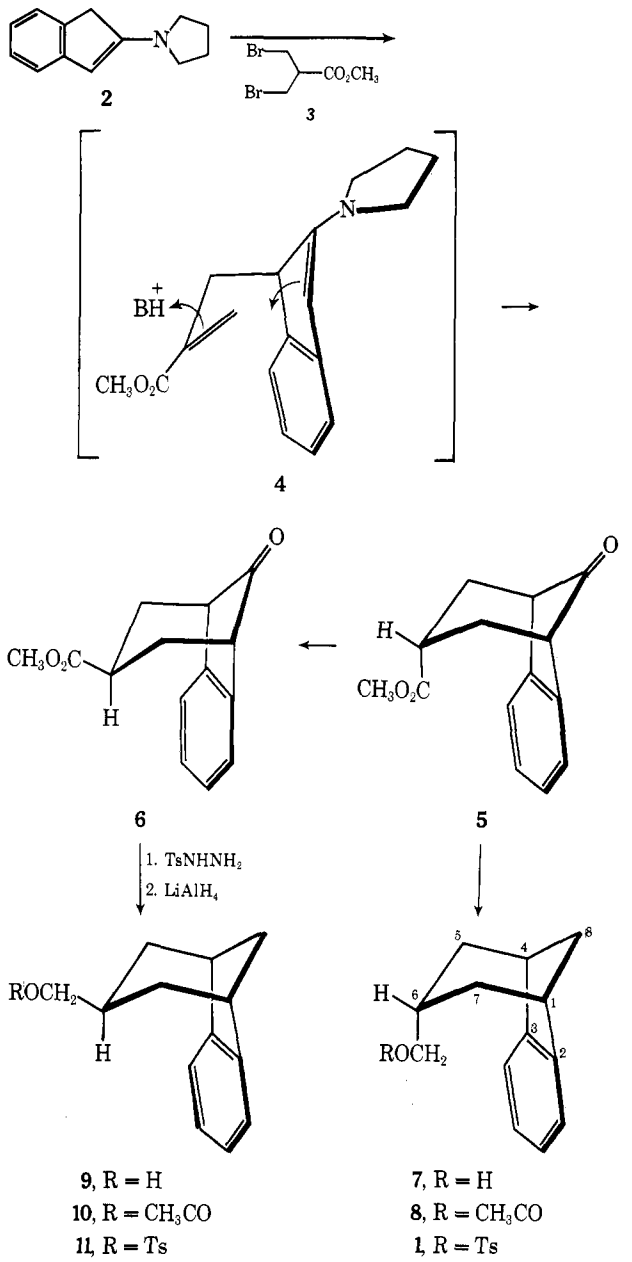
The severe diaxial interactions in the endo methyl tosylate **1** might cause it to have a significant population of the boat conformation **1a**, destroying the geometry appropriate for



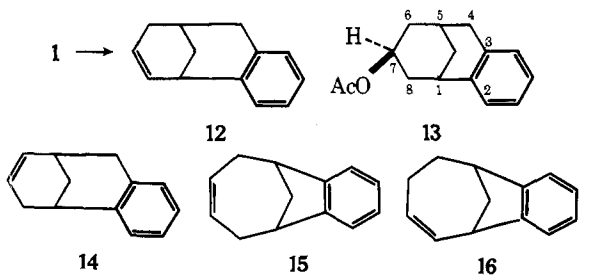
1a

participation. Such a conformation is developed in the corresponding bicyclo[3.3.1]nonanone methyl derivatives.[3c] Nevertheless both the solvolytic data and ^1H NMR of endo tosylate **1** at room temperature and low temperature suggest that it exists predominantly in the chair form **1**. Protons of the methylene bearing the tosylate, in endo epimer **1**, occur 1.1 ppm upfield of those in the epimeric exo tosylate **11** and are unchanged to −80 °C in acetone. There is also evidence from lactonization experiments on other members of the benzobicyclo[3.2.1]octenyl series that the chair form is the predominant conformation.[3b]

The suitability of the architecture of endo tosylate **1** for participation was reflected by both its enhanced rate and by its products of acetolysis which were completely rearranged. Acetolysis of bicyclic endo methyl tosylate **1** at 75 °C proceeded with a rate of 2.3×10^{-5} s^{-1}, 58 times faster than the corresponding exo methyl tosylate **11** and 100 times faster than isobutyl tosylate.[8] The products of endo methyl tosylate

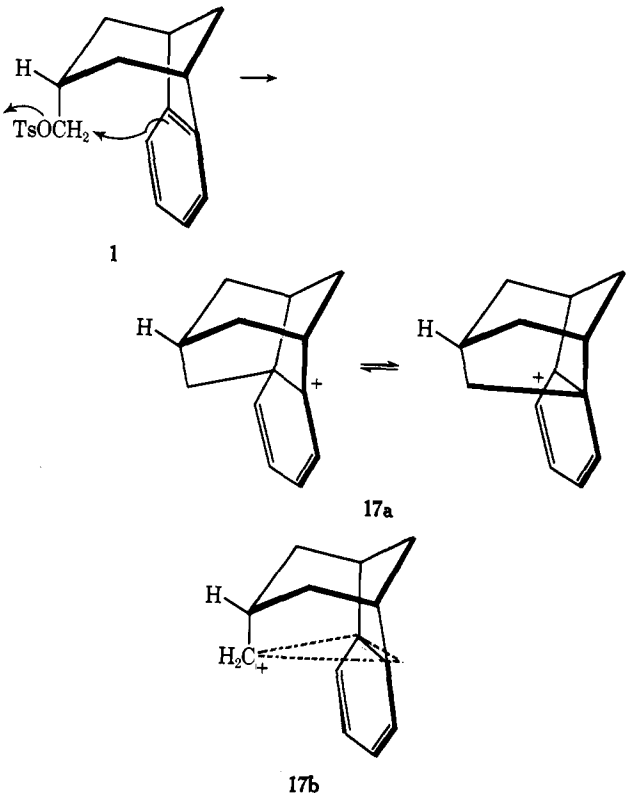


1 acetolysis were of completely rearranged structure. None of the unrearranged acetate 8 was detected in the solvolysis mixture (limit about 2%) which was composed only of olefin 12 and acetate 13 in a ratio of 3:7.5. The proposed structures



of the solvolysis products are supported by spectral data. Olefin 12 is consistent with its ^{1}H NMR which showed two vinyl protons, four aromatic, five allylic or benzylic protons, and three aliphatic protons. The observation of three aliphatic protons (δ 2.1–1.7) appeared to eliminate the isomeric olefin 14. This conclusion is in accord with reported NMR data for bicyclo[3.3.1]nona-2,6-diene.[9] Similar arguments rule out olefins 15 and 16. Both the VPC behavior and single acetate methyl at δ 1.93 suggested the formation of only one epimer at carbon 7 for 13 and the stereochemistry of the acetate follows from mechanistic considerations as well as its NMR.

A mechanism consistent with these results is ionization of tosylate 1 with concomitant formation of species 17a and/or 17b.



Because the position of the developing cation above the aromatic ring is fixed directly between the two participating carbons in 1, the contribution of form such as 17b as an intermediate may be enhanced over that of 17a. Such symmetry as in 1 may require a somewhat different mode of participation than that required for Ar_1-5 or Ar_2-6[10] participation alone.

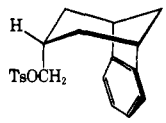
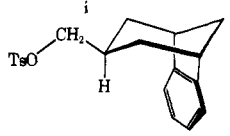
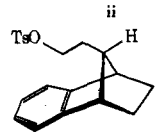
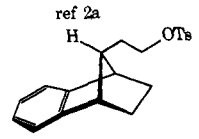
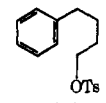
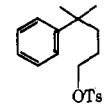
The stabilized ion 17 could have taken several routes to restore the aromaticity of the participating phenyl nucleus. Elimination of axial hydrogens at carbons 6 or 8 could yield olefins 12 and/or 14. The reason for the formation of only olefin 12 is not apparent.

Alternatively, the ion 17 could be attacked directly by an acetate nucleophile at carbons 4 or 7. Absence of acetate 8 in the solvolysis mixture ruled out any observable attack at carbon 4. Exclusive rearrangement of the bridged ion 17 is consistent with the labeling experiments of Jackman and co-workers.[11] Acetate attack at carbon 7 of ion 17 should lead to the exo stereochemistry proposed for acetate 13.

The rate of acetolysis of endo tosylate 1 also supports the presence of participation in the rate-determining ionization process. The acetolysis of exo tosylate 11, which gives only the nucleophilic displacement product, acetate 10, proceeds at a much slower rate. Absolute and relative rates of acetolysis of this and other relevant aryl tosylates are accumulated in Table I. While consistent with the rate observed for a simple model, isobutyl tosylate, the solvolysis rate of exo tosylate 11 is probably not an ideal comparison rate for the endo tosylate 1 because of the greater distance of the function from the aromatic ring. While the steric environment of the endo tosylate 1 is such that solvolytic displacement by acetate is severely impeded if not impossible, the rate observed for 11 is likely due only to displacement.

A rearrangement–internal return pathway followed by a slower acetolysis of the rearranged sulfonate was not signifi-

Table I. Rates of Acetolysis at 75 °C

X = OTs	s^{-1}	Relative	k_{endo}/k_{exo}
	2.3×10^{-5}	100	Δ 58
i 	4×10^{-7}	1.7	
ii  ref 2a	7.3×10^{-6}	32	Δ 9.7
 ref 2a	7.7×10^{-7}	3.3	
 ref 2b	4.8×10^{-7}	2	
 ref 2c	6.3×10^{-7}	2.7	
 ref 8	2.3×10^{-7}	1	

cantly affecting the rate of acetolysis of compound 1. The acetolysis rate could be easily monitored by NMR using perdeuterioacetic acid solvent at 59 °C. Comparison of the rate of appearance of the methyl signal of *p*-toluenesulfonic acid (δ 2.4), the rate of formation of the distinctive signal for the aromatic portions of 12 and 13 (δ 7.1), and the rate of disappearance of both the methyl signal of the *p*-toluenesulfonate (δ 2.5) and the aromatic singlet (δ 6.9) of starting tosylate 1 proved the concomitant rearrangement and solvolysis. The rate obtained by this study was comparable to that obtained by titration at the higher temperature (about 8×10^{-6} s^{-1} at 58 °C).

Though the difference in relative rates between 1 and 11 is not highly dramatic (endo/exo rate ratio of 59) compared with double bond rate ratios, this example gives some suggestion of the maximum rate expected in primary carbon participation of aromatics without activating substituents. The previous maximum rate ratio for aromatic participation was observed by Tanida and Muneyuki[2] having a participation rate ratio of 9.7 (endo/exo) (Table I). Their example, having an ethyl side chain, has more degrees of freedom.

Experimental Section

General. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Proton magnetic resonance spectra were obtained on Varian Associates T-60 and T-60A instruments and a JEOL JNM PS-100 spectrometer. Mass spectra were obtained on an Associated Electrical Industries MS-902. Infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer. Vapor-phase chromatography was performed on a Varian Aerograph Model 90-P3 instrument using the following columns: A, 5% SE-30 on Chromosorb G, 0.25 in. × 6 ft; B, 5% SE-30 Chromosorb G, 0.25 in. × 1.5 ft. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Spectral data were obtained as follows: NMR as solutions in deuteriochloroform (units in parts per million downfield from internal Me_4Si); ir as solutions in chloroform or deuteriochloroform (units in cm^{-1}, calibrated with the 1601-cm^{-1} polystyrene absorbance); *m/e* 70 eV.

Methyl Benzobicyclo[3.2.1]octen-8-one-3-*endo*-carboxylate (5). To a solution of 27.7 g (0.150 mmol) of the pyrrolidine enamine of 2-indanone 2 and 30.4 g (0.30 mmol) of triethylamine in dry methanol (300 ml) was added 39.0 g (0.15 mmol) of methyl β,β′-dibromoisobutyrate over a 10-min period. The resulting solution was heated to reflux under nitrogen for 3 h, water (75 ml) added, and the mixture allowed to cool to ambient temperature for 2 h. Water (225 ml) was then added to the reaction mixture and the resulting solution extracted with chloroform (5 × 100 ml). The combined chloroform extracts were washed with 10% HCl (2 × 300 ml), saturated $KHCO_3$ (2 × 250 ml), and saturated NaCl (2 × 250 ml) and dried (Na_2SO_4). The solvent was removed to yield a dark oil which was taken up in chloroform and filtered through alumina, and the resulting solution taken to dryness. The material obtained from the alumina filtration was sublimed (100–107 °C at 0.1 mm) to yield 9.7 g (28%) of the benzobicyclo[3.2.1]cyclooctenyl ester 5: mp 106–108 °C; ir 1720, 1760 cm^{-1}; NMR δ 3.6 (s, 3 H, OCH_3), 7.25 (s, 4 H, Ph); *m/e* 230.

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.14; H, 6.16.

Methyl Benzobicyclo[3.2.1]octen-8-one-3-*exo*-carboxylate (6). To a solution of 3 mmol of sodium methoxide in methanol (12 ml) was added 690 mg (3 mmol) of the endo ester 5. The solution was heated to reflux under nitrogen for 34 h. The cooled reaction mixture was acidified with 5% acetic acid and the resulting solution was extracted with methylene chloride (30 ml). The methylene chloride solution was washed with 5% $KHCO_3$ (10 ml) and dried (Na_2SO_4). The solvent was removed to yield 547 mg (79%) of the exo ester 6: mp 105–108 °C; ir 1760, 1725 cm^{-1}; NMR δ 3.64 (s, 3 H, OCH_3), 7.25 (s, 4 H, Ph); *m/e* 230.

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13. Found: C, 73.14; H, 6.16.

Benzobicyclo[3.2.1]octenyl-*endo*-methyl Alcohol (7). To a solution of 920 mg (4 mmol) of the endo ester 5 in tetrahydrofuran (THF) (10 ml) was added 800 mg (4.3 mmol) of *p*-toluenesulfonylhydrazine and 5 drops of acetic acid. The solution was allowed to stand at ambient temperature for 25 h, then the solvent was removed and the tosylhydrazone dried in vacuo to give a white solid foam which showed no ketone absorbance (1760 cm^{-1}) in the ir. To a slurry of $LiAlH_4$ (600 mg) in dry THF was added a solution of the tosylhydrazone in THF (15 ml). The resulting mixture was heated to reflux under nitrogen for 24 h, an additional 100 mg of $LiAlH_4$ added, and the reflux continued for 58 h. The excess hydride was quenched by the addition of ethyl acetate followed by saturated NH_4Cl (10 ml) and the resulting solution stirred at ambient temperature for 0.5 h. The granular precipitate was filtered and washed with methylene chloride (50 ml) and ether (40 ml). The combined organic solutions were washed with 2 N HCl (50 ml), saturated $KHCO_3$ (50 ml), and saturated NaCl (40 ml) and dried (Na_2SO_4). The solvent was removed to yield 460 mg (65%) of the crude alcohol 7 as an oil: ir 3590, 2920 cm^{-1}; NMR δ 2.2 (m, 2 H), 3.1 (m, 2 H), 7.11 (s, 4 H, Ph); *m/e* 188. Attempted preparation of an analytical sample of the alcohol by VPC failed, apparently owing to decomposition. An acceptable analysis was obtained on the acetate derivative 8.

Benzobicyclo[3.2.1]octenyl-*exo*-methyl Alcohol (9). To a solution of 890 mg (3.9 mmol) of the exo keto ester 6 in tetrahydrofuran (THF) (10 ml) was added 745 mg (4.0 mmol) of *p*-toluenesulfonylhydrazine and 5 drops of acetic acid. The resulting solution was allowed to stand at ambient temperature for 24 h, then the solvent was removed and the tosylhydrazone dried in vacuo. To a slurry of 800 mg of $LiAlH_4$ in dry THF was added a solution of the tosylhydrazone in THF (10 ml). The resulting mixture was heated to reflux, under nitrogen, for 44 h, an additional 200 mg of $LiAlH_4$ added, and the reflux continued for 84 h. The reaction mixture was processed as in the preparation of alcohol 7 to yield 658 mg (90%) of the exo methyl alcohol 9 as an oil: ir 3590, 2920 cm^{-1}; NMR δ 3.39 (d, 2 H), 7.18 (s, 4 H, Ph); *m/e* 188. Again attempted preparation of an analytical sample by VPC failed, apparently owing to decomposition of the alcohol. An acceptable analysis was obtained for the acetate derivative 10.

Benzobicyclo[2.1.1]octenyl-3-*endo*-methyl Tosylate (1). To an ice-cooled solution of 500 mg (2.7 mmol) of endo alcohol 7 in dry pyridine (7.5 ml) was added 1.02 g (5.3 mmol) of *p*-toluenesulfonyl chloride. An immediate color change was noted as a reddish-yellow color appeared. The solution, in a stoppered Erlenmeyer flask, was allowed to stand in a refrigerator for 210 h. The reaction mixture was poured into 30 ml of ice water and the mixture was stirred until the

ice melted. The aqueous mixture was extracted with ether (75, 25 ml) and the combined ether extracts were washed with cold 2 N HCl (2 × 30 ml), water (20 ml), and saturated NaCl (20 ml) and dried (Na_2SO_4). The solvent was removed to yield 821 mg (90%) of the crude tosylate 1. The tosylate was recrystallized from pentane–ether: mp 59–61 °C; ir 1175, 1190 cm^{-1}; NMR δ 2.43 (s, 3 H), 6.98 (s, 4 H, Ph); *m/e* 342.

Anal. Calcd for $C_{20}H_{22}O_3S$: C, 70.08; H, 6.47. Found: C, 69.78; H, 6.16.

Benzobicyclo[3.2.1]octenyl-3-*exo*-methyl Tosylate (11). To an ice-cooled solution of 323 mg (1.7 mmol) of exo alcohol **9** in dry pyridine (5 ml) was added 665 mg (3.5 mmol) of *p*-toluenesulfonyl chloride. An immediate color change occurred and a bright yellow color was noted. The resulting mixture was processed as in the preparation of the endo tosylate 1 to give 525 mg (90%) of crude exo tosylate 11 which was purified by recrystallization from pentane–ether: mp 60–62 °C; ir 1175, 1190 cm^{-1}; NMR δ 2.42 (s, 3 H, CH_3), 3.13 (m, 2 H), 3.77 (d, 2 H, CH_2O–), 7.10 (s, 4 H, Ph); *m/e* 342.

Anal. Calcd for $C_{20}H_{22}O_3S$: C, 70.08; H, 6.47. Found: C, 69.80; H, 6.36.

Acetate Derivative (8) of Endo Alcohol 7. To a solution of 100 mg of endo alcohol **7** in acetic anhydride (2 ml) was added 10 drops of pyridine and the resulting solution heated to 70 °C under nitrogen for 18 h. The reaction mixture was poured into water (25 ml) and the resulting aqueous solution was extracted with ether (30 ml). The ether extract was washed with 2 N HCl (20 ml), saturated $KHCO_3$ (20 ml), and saturated NaCl (15 ml) and dried (Na_2SO_4). The solvent was removed to yield 118 mg of acetate **8** as an oil. An analytical sample was obtained by preparative VPC on column A: ir 170 cm^{-1}; NMR δ 1.90 (s, 3 H, CH_3CO–), 2.75 (d, 2 H), 3.10 (m, 2 H), 7.17 (s, 4 H); *m/e* 230.

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.83. Found: C, 78.40; H, 7.83.

Acetate Derivative (10) of Exo Alcohol 9. To a solution of 100 mg of alcohol **10** in acetic anhydride (2 ml) was added 10 drops of pyridine and the resulting solution was heated to 80 °C under nitrogen for 14 h. The reaction mixture was processed as in the preparation of acetate **8** to yield 45 mg of the exo acetate **10** as an oil. An analytical sample was obtained by preparative VPC on column A: ir 1715 cm^{-1}; NMR δ 1.93 (s, 3 H, CH_3CO), 3.10 (m, 2 H), 3.80 (d, 2 H, CH_2O–), 7.10 (s, 4 H, Ph); *m/e* 230.

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.83. Found: C, 78.19; H, 7.86.

Acetolysis of Endo Tosylate 1. A solution of 105 mg (0.3 mmol) of tosylate 1 in glacial acetic acid (1.4 ml) was sealed in a ampule and heated at 75 °C for 12 h. The cooled reaction mixture was poured into water (10 ml) and methylene chloride (20 ml). The organic phase was washed with saturated $KHCO_3$ (10 ml) and saturated NaCl (10 ml) and dried (Na_2SO_4). The solvent was removed to yield 81 mg of a crude oil which was a mixture of acetate **13** and olefin **12** in the approximate ratio 7.5:3 (determined by VPC) and also contained some unreacted tosylate 1 (NMR). Analytical samples were obtained by preparative VPC on columns A and B.

Acetate **4**: ir 1720 cm^{-1}; NMR δ 1.93 (s, 3 H, CH_3CO), 4.93 (m, 1 H, HCO–); *m/e* 230.

Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.83. Found: C, 78.53; H, 7.96.

Olefin **3**: ir 3015 cm^{-1}; NMR δ 5.67 (m, 2 H, HC=CH), 7.07 (s, 4 H, Ph); *m/e* 170.

Anal. Calcd for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.55; H, 8.45.

Acetolysis of Endo Tosylate 1 in Deuterioacetic Acid. A 30-mg sample of tosylate 1 was dissolved in 0.5 ml of deuteroacetic acid in an NMR tube. Immediate scan of the mixture at the temperature of the probe (35 °C) showed no new peaks. Scans at 10, 20, and 40 min showed no changes. After 12 h the spectrum remained essentially unchanged. The NMR tube was then heated in a refluxing chloroform bath. The tube was withdrawn from the bath at intervals and quenched in ice water. The spectrum scan showed the development of the *p*-toluenesulfonic acid methyl singlet at 2.40 ppm and the disappearance of the methyl singlet of 1 at 2.5 ppm. The aromatic signal of 1 at δ 6.95 disappeared and the characteristic multiplet observed for the benzobicyclo[3.3.1]nonane system appeared. At the same time the multiplet for the unshielded O–CH hydrogen of the [3.3.1] system appeared at δ 4.8. Crude rate measurements indicated a $t_{1/2}$ of about 1400–1500 min for each of these processes which compares with the titrimetric rate. VPC of the final mixture showed both olefin **12** and acetate **13**.

Acetolysis of Exo Tosylate 11. A 0.03 M solution of exo tosylate **11** in glacial acetic acid was heated at 75.0 °C to 50% completion. The reaction mixture was processed as in the acetolysis of endo tosylate 1. The material isolated was identical by NMR and VPC with a mixture of exo tosylate 11 and exo acetate **10**.

Rate Measurements. The procedure used for determination of solvolysis rates is that of Winstein.[12] Aliquots of a 0.032 M solution of endo tosylate 1 in glacial acetic acid, containing 1% by weight acetic anhydride, were sealed in ampules and placed in an oil bath thermostatted at 75.0 °C (±0.1 °C) Ampules were removed at appropriate intervals and immersed in ice. The ampule was then allowed to warm to room temperature and a 5.0-ml aliquot removed and titrated with 0.05 M sodium acetate to a bromophenol blue end point. The rate was followed to ~85% completion and the plot of log (C_0/C_t) vs. time was computed. A regression analysis of the ln (C_0/C_t) as a function of time yielded the rate, $k = 2.28\ (\pm 0.07) \times 10^{-5}\ s^{-1}$.

The identical procedure was used for the exo tosylate **11**. The plot of log (C_0/C_t) against time followed by a regression analysis of ln (C_0/C_t) as a function of time gave the rate, $k = 4.0\ (\pm 0.3) \times 10^{-7}\ s^{-1}$.

Registry No.—1, 58426-32-7; **2**, 39157-79-4; **3**, 22262-60-8; **5**, 55529-62-9; **6**, 55511-69-8; **7**, 58426-33-8; **8**, 58426-34-9; **9**, 58462-39-8; **10**, 58462-40-1; **11**, 58462-41-2; **12**, 58426-35-0; **13**, 58426-36-1; sodium methoxide, 124-41-4; *p*-toluenesulfonylhydrazine, 1576-35-8; *p*-toluenesulfonyl chloride, 98-59-9; acetic anhydride, 108-24-7.

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