Kinetic Measurements. The experimental procedure was identical with that described previously.[12] The temperatures of 0, 25, and 48.6° were controlled to within ±0.02°. The temperature of the bath for the −43.7° determination (7-norbornenone) was maintained by immersing the bath (a Dewar vessel) into another bath which was cooled to −43.7° and maintained there by addition of Dry Ice, using a sulfur dioxide gas thermometer to follow the temperature.

In most cases the concentrations of the reactants were maintained at 0.16 *M* ketone and 0.02 *M* sodium borohydride. Usually, several kinetic runs were conducted for each temperature and the mean values are reported in Table II. Generally there was no difficulty in obtaining reproducible values to within 2 to 3%. For example, four successive determinations for 2-norbornanone yielded the values at 25.0° of ($k_2 \times 10^4$, l. mole^{-1} sec^{-1}) 24.5, 24.0, 23.8, and 23.3, with an average value of 24.0.

Most runs were made at 0 and 25°. In the case of 7-norbornenone the rate at 0° was so fast that it represents close to the practical limit of measurement by the usual technique. Accordingly, to determine the temperature coefficient of the rate, it was necessary to select a lower temperature. The experimental difficulties result in a much larger experimental uncertainty in these values than those determined by the standard kinetic procedure.

The rate of reaction of 7-norbornenone was far too fast for the usual technique. Accordingly, its rate was determined by two approximate procedures. First, precooled solutions (0°) of the borohydride and the ketone in the two limbs of a U-shaped vessel were rapidly mixed by tilting and shaking vigorously. After a measured time interval, of the order of 30 to 60 sec, the reactions were quenched by the addition of aqueous acid. Analysis yielded the ketone/alcohol ratio for calculation of the rate constant. In a second procedure, borohydride was added to a mixture of benzaldehyde and 7-norbornanone. Gas chromatographic analysis of the product provided the data to estimate the relative magnitudes of the rate constants. Since the value for benzaldehyde is known,[12] it was possible to calculate the value for 7-norbornanone. The two approaches yielded values which agreed with each other to within 20%.

Product Measurements. Vapor phase chromatography was used for all analyses and the retention times were compared with authentic samples. The only exceptions were *syn*-7-norbornenol and both *exo*- and *endo*-7,7-dimethylnorborneols, which were not available. Reduction of 7-norbornenone produced two products in a ratio of 85:15. The 85% product was identical with authentic *anti*-7-norbornenol. The minor peak was therefore assigned to the *syn* isomer. In the other case, 7,7-dimethyl-2-norbornanone was reduced by lithium aluminum hydride. Two products were formed in a ratio of 91:9. Camphor likewise yielded two products in a ratio of 90:10. In the latter case there was no difficulty in identifying the major product, 90%, as isoborneol, and the minor as borneol. The assumption was made that the 91:9 distribution in 7,7-dimethyl-2-norbornanone likewise corresponded to preferential *endo* attack.

For the analyses, we utilized a Perkin-Elmer Model 226 vapor phase chromatograph employing a 150 ft × 0.01 in. i.d. Ucon LBX-500 column, with block temperature at 260°, flame ionization detector at 160°, 20 psi, programed at 40° (5 min)–140° (15 min) at 10°/min. This instrument proved very effective in permitting us to analyze the reaction mixtures directly, without prior removal of the isopropyl alcohol.

Acknowledgment. It is a pleasure to acknowledge the contribution of one of the referees who, on three successive occasions, requested amplification and extension of the discussion and arguments, thereby making possible this unusually detailed treatment of the factors influencing the behavior of rigid bicyclic systems.

The Synthesis and Solvolysis of 7-Ketonorbornyl Tosylates[1]

Paul G. Gassman and James L. Marshall[2]

Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received January 13, 1966*

Abstract: *exo*- and *endo*-2-hydroxybicyclo[2.2.1]heptan-7-one have been synthesized; their stereochemistry has been rigorously proven by a combination of chemical and spectroscopic methods. The tosylate of these epimeric alcohols have been prepared. Under the usual acetolysis conditions, the *endo* tosylate solvolyzed 6.0 times faster than the *exo* tosylate. Both tosylates yielded a mixture of *exo*- and *endo*-2-acetoxybicyclo[2.2.1]heptan-7-one. However, the product ratio was not the same for both the *exo* and the *endo* tosylate solvolyses. The implications of these results on bicyclic carbonium ion theory are discussed.

The importance of nonclassical carbonium ions in solvolysis reactions continues to be the subject of intensive investigations.[3,4] Of particular relevance are the studies of the solvolytic behavior of bicyclic tosylates, especially the well-known investigations of the acetolysis of bicyclo[2.2.1]heptyl tosylates.[5] We report here on the effect of the carbonyl function on the acetolysis of 2-*exo*-hydroxybicyclo[2.2.1]heptan-7-one tosylate (**1**) and 2-*endo*-hydroxybicyclo[2.2.1]heptan-7-one tosylate (**2**).

Synthesis and Stereochemistry

The starting material for the synthesis of 2-*exo*-hydroxybicyclo[2.2.1]heptan-7-one (**3**) was 7,7-dimethoxybicyclo[2.2.1]heptane (**4**).[6] Epoxidation of **4** with perbenzoic acid gave 7,7-dimethoxybicyclo-[2.2.1]heptane *exo*-2,3-epoxide (**5**) in 87% yield. Although models suggest that the *exo* side of the double bond in **4** is more hindered than the *endo* side, the attacking reagent reacted from the *exo* position. The direction of this stereospecific epoxidation is probably due to hydrogen bonding of the attacking peracid with the oxygen of the 7-methoxyl group.[7] When **5** was reduced

(1) Part of this paper has appeared in preliminary form: P. G. Gassman and J. L. Marshall, *J. Am. Chem. Soc.*, **87**, 4648 (1965); *Tetrahedron Letters*, No. 46, 4073 (1965).

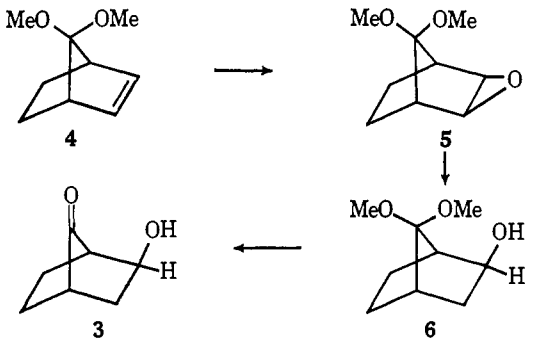
(2) National Science Foundation Cooperative Predoctoral Fellow, 1962–1963, 1964–1966.

(3) H. C. Brown, "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962.

(4) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

(5) J. A. Berson, "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p 111.

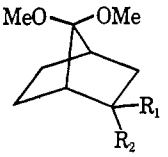
(6) P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).



with lithium aluminum hydride in refluxing tetrahydrofuran for 12 days, the alcohol **6** was obtained in 94% yield. The stereochemistry of **6** was established on the basis of near-infrared and nmr spectroscopy and chemical reactions. Absorption at 1.442 μ in the near-infrared spectrum of **6** (dilute carbon tetrachloride solution) indicated the presence of a strong internally hydrogen-bonded hydroxyl group.[8] A near-infrared spectrum of the epimeric alcohol **7** under identical conditions showed only a free hydroxyl stretching frequency overtone at 1.412 μ.

Nuclear magnetic resonance spectroscopy gave additional confirmation of the stereochemical assignments. One use of nmr was to establish the positions of the methoxyl group as shown in Table I. Whereas 7,7-dimethoxybicyclo[2.2.1]heptane (**8**), 2-*exo*-acetoxy-7,7-dimethoxybicyclo[2.2.1]heptane (**9**), 2-*endo*-acetoxy-7,7-dimethoxybicyclo[2.2.1]heptane (**10**), and 2-*endo*-hydroxy-7,7-dimethoxybicyclo[2.2.1]heptane (**7**) have virtually identical chemical shifts for the methoxyl protons, 2-*exo*-hydroxy-7,7-dimethoxybicyclo[2.2.1]-heptane (**6**) exhibits a considerable downfield shift. This shift signalizes the effect of internal hydrogen bonding between the *syn*-methoxyl and the *exo*-hydroxyl groups.

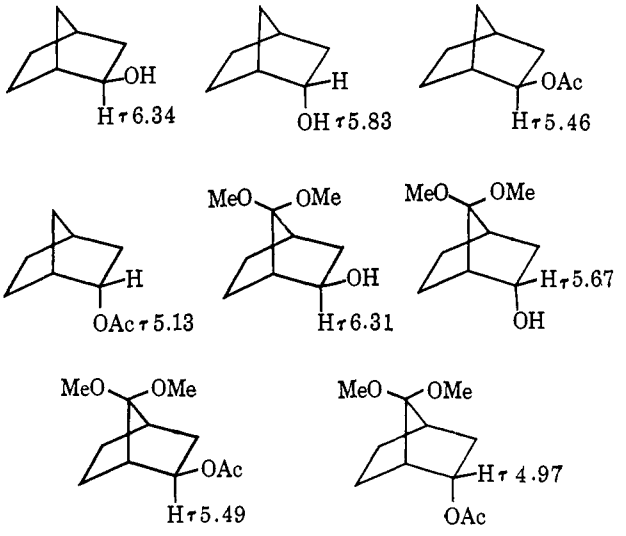
Table I



R_1	R_2	OMe	OMe
H	H	6.82	6.82
H	OAc	6.80	6.80
OAc	H	6.80	6.81
H	OH	6.78	6.79
OH	H	6.69	6.74

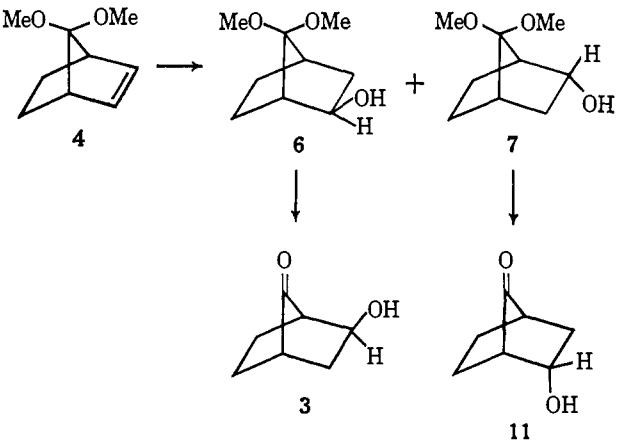
Further evidence for stereochemical assignments was obtained from the position of the α hydrogens in the nmr spectra of the epimeric alcohols and acetates. Wong and Lee have shown[9] that the *endo* α hydrogens appear at much higher field than the *exo* α hydrogens in norborneols and norbornyl acetates. A comparison of the published[9] data with our values is shown in Scheme I. Thus the spectroscopic evidence seems

Scheme I



conclusive in itself.

Chemical evidence for the *exo* stereochemistry of the hydroxyl group in **6** has been adduced in several ways. Hydroboration of **4** according to the method of Brown and Subba Rao[10] gave a 22:78 mixture of ketal alcohols in 74% yield. Vapor phase chromatography on Carbowax 20-M showed that the major component had a much shorter retention time than the minor component. This finding indicated that the major component was the internally hydrogen bonded *exo* epimer.[11] Separation of the isomeric alcohols by vapor phase chromatography and recrystallization gave pure samples of **6** and **7**.



Lithium ethylamine reduction of 7,7-dimethoxybicyclo[2.2.1]heptane *exo*-2,3-epoxide (**5**) also yielded a small amount of **6**. However, a second component

(7) Several examples of stereospecific epoxidation apparently involving hydrogen bonding have appeared: H. B. Henbest and R. A. L. Wilson, *J. Chem. Soc.*, 1958 (1957); H. B. Henbest and B. Nicholls, *ibid.*, 4608 (1957); K. V. Scherer, Jr., Thesis, Harvard University, 1962. We wish to thank Dr. Scherer for informing us of his results prior to publication.

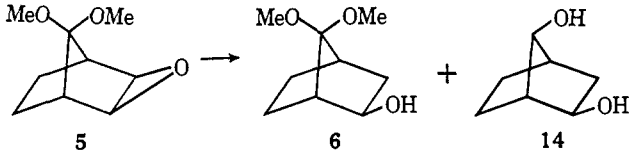
(8) R. Piccolini and S. Winstein, *Tetrahedron Letters*, No. 13, 4 (1959).

(9) E. W. C. Wong and C. C. Lee, *Can. J. Chem.*, **42**, 1245 (1964).

(10) H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957).

(11) The danger of attempting to establish stereochemistry on the basis of glpc retention times *alone* has been discussed in the literature: K. Mislow and J. G. Berger, *J. Am. Chem. Soc.*, **84**, 1956 (1962), have shown that in the case of internal hydrogen bonding between alcohol and olefin functions the relative order of retention times in special cases may be a function of the column substrate. Thus the unqualified generalization that internal hydrogen bonding is accompanied by shorter glpc retention times should not be used as the sole basis for the definitive assignment of stereochemistry.

of the reduction mixture was bicyclo[2.2.1]heptane-*exo*-2-*syn*-7-diol (**14**) which was identical with an

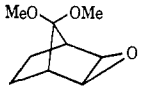
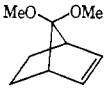
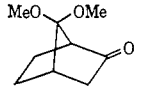
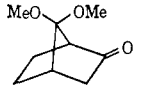
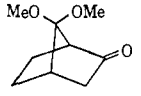


5 **6** **14**

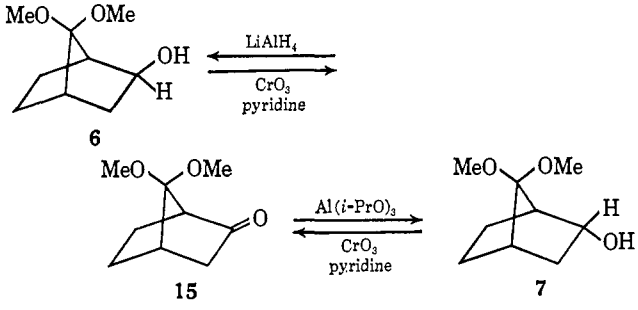
authentic sample.[12]

Having firmly established the stereochemistry of the hydroxyl group in **6**, we explored various methods of preparing large amounts of the pure epimers of 7,7-dimethoxybicyclo[2.2.1]heptan-2-ol. The experimental results are summarized in Table II. The pure *exo* isomer was most conveniently prepared by the lithium aluminum hydride reduction of the ketal epoxide **5**, while the epimeric *endo* alcohol was readily obtained by Meerwein–Ponndorf–Verley reduction of the ketone **15**. Both of these epimeric alcohols could be oxidized to **15**.

Table II. Preparation of 7,7-Dimethoxybicyclo[2.2.1]heptan-2-ols

		% *endo*	% *exo*	% yield
	$LiAlH_4$	0	100	94
	1. B_2H_6 2. $OH^\ominus$, H_2O_2	22	78	74
	$LiAlH_4$	25	75	77
	Na, EtOH	30	70	42
	$Al(i\text{-}PrO)_3$, *i*-PrOH	98[a]	2[a]	91

[a] See Experimental Section.



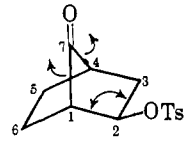
6 **15** **7**

The ready availability of **6** and **7** at this stage permitted further progress. Hydrolysis of these pure epimeric alcohols gave the corresponding keto alcohols **3** and **11**. Acetylation of **3** and **11** with acetyl chloride in pyridine yielded the expected acetates **12** and **13**, respectively. The keto alcohols were converted to their corresponding tosylates **1** and **2**, according to the procedure of Tipson.[13]

Spectral data indicated that no structural changes had occurred during the hydrolysis of **6** and **7** or during acetate or tosylate formation. The infrared spectra of **3**, **11**, **12**, **13**, **1**, and **2** all showed the carbonyl absorption centered at *ca.* 5.62 μ which is characteristic of 7-keto-norbornane derivatives.[6] In addition, nmr spectra of the keto acetates and keto tosylates were consistent with the assigned structures (see Experimental Section). It should also be noted that lithium aluminum hydride reduction of **12** yielded the known diol **14**.[12]

Solvolysis Results

The solvolysis of *exo*-2- and *endo*-2-hydroxybicyclo-[2.2.1]heptan-7-one tosylates was carried out in anhydrous acetic acid at 75, 90, and 100°. The specific rate constants are listed in Table III. Included in Table III are the absolute rate constants for the solvolyses of related tosylates. It must be stressed at this point that comparison of the absolute rates of solvolyses of the 7-keto compounds with other absolute rate constants is complicated by the inductive effect of the carbonyl and the change in geometry of the system which results from the incorporation of the carbonyl in the 7 position. Whereas the electron-withdrawing carbonyl group would tend to decrease the rate of solvolysis, the presence of an sp^2-hybridized center at C-7 would tend to flare the C_1–C_7–C_4 angle. This



16

would result in an increase of the C_1–C_2–C_3 angle as shown in **16**. This increased bond angle would make the ground state more like the transition state and thus increase the rate of solvolysis. The fact that both **1** and **2** solvolyze at approximately the same rate as **18** indicates that a fortuitous canceling of the opposing effects of bond angle change and inductive effect may be occurring in **1** and **2**.

Vapor phase chromatography indicated that **1** gave a mixture of acetates consisting of 40% *endo* acetate **13** and 60% *exo* acetate **12** on acetolysis. A similar product analysis on the solvolyzed *endo* tosylate **2** indicated the presence of 2.3% of **13** and 97.7% of **12**.[14]

Discussion of Results

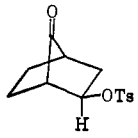
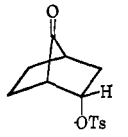
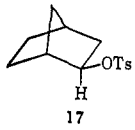
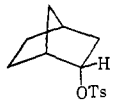
Much of the attention accorded the solvolysis of various derivatives of bicyclo[2.2.1]heptane[5] has been directed toward establishing the existence[17] or non-existence[18] of a nonclassical carbonium ion intermediate in the solvolysis of 2-substituted bicyclo[2.2.1]heptanes. Results obtained from the solvolysis of bicyclo[2.2.1]-heptyl tosylates in which the bicyclic system was substituted with groups capable of stabilizing a positive charge (*i.e.*, methyl or phenyl) have been used as evidence both for and against the existence of nonclassical

(12) We wish to thank Dr. Jack Crandall for supplying us with an authentic sample of this diol.

(13) R. S. Tipson, *J. Org. Chem.*, 9, 235 (1944).

(14) These values have been corrected for the relationship between peak area and per cent composition with the vpc response of mixtures of known composition.

Table III. Acetolysis Rates of Various Norbornyl Tosylates

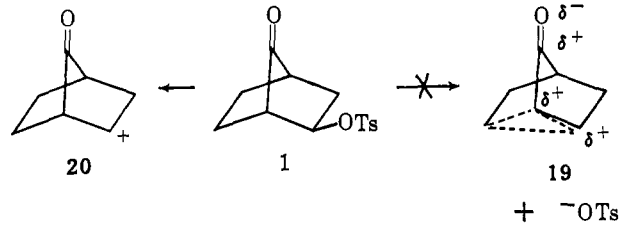
Compound	Ref	Temp, °C	Rate, sec^{-1}	ΔH^*, kcal/mole	ΔS^*, eu
 1		100.00	$(1.84 \pm 0.01) \times 10^{-4}$ [16]	27.1	−3.5
		90.00	$(5.96 \pm 0.06) \times 10^{-5}$		
		75.71	$(1.33 \pm 0.01) \times 10^{-5}$		
		(25.0)	1.44×10^{-8}		
 2		100.00	$(4.66 \pm 0.00) \times 10^{-4}$	24.7	−8.1
		90.00	$(1.79 \pm 0.03) \times 10^{-4}$		
		75.74	4.28×10^{-5}		
		(25.0)	8.66×10^{-8}		
 17	15	25	2.33×10^{-5}	21.6	−7.2
 18	15	(25)	8.28×10^{-8}	25.8	−4.4

carbonium ions. Since stabilizing the positive charge yielded data which were inconclusive, we felt that destabilizing the norbornyl cation might lead to more definitive results.

In considering the large *exo/endo* rate ratio which is generally observed in the solvolysis of norbornyl tosylates, the two published explanations of this phenomenon require comment.[3-5,17-19] According to one postulate the norbornyl cation exists as a rapidly equilibrating pair of classical ions,[3,19] with both *exo*- and *endo*-norbornyl tosylates undergoing initial ionization to a classical cation. The fact that the *exo* isomer solvolyzes 10^2–10^3 times faster than the *endo* isomer has been rationalized by the hypothesis that the *endo* isomer is abnormally slow due to steric hindrance to ionization of the *endo* tosylate in the 2 position by the *endo* hydrogen in the 6 position.[3,19] The alternate hypothesis is that the large *exo/endo* rate ratio observed for the solvolyses of norbornyl tosylates is due to anchimeric assistance by the 1–6 σ electrons in the solvolysis of the *exo* isomer.[4,5,17]

If both *exo*- and *endo*-norbornyl tosylates initially solvolyze to the same classical carbonium ion, the presence of a carbonyl function in the 7 position should have relatively little effect on the inhibition of solvolysis by the C-6 *endo* hydrogen. Thus the *exo/endo* rate ratio for **1** and **2** should be 10^2–10^3 *barring other effects.*

Alternatively, if the norbornyl *exo/endo* rate ratio is due to anchimeric assistance, the presence of a carbonyl function at C-7 would be expected to have drastic effects. The solvolysis of **1** should lack the rate enhancement characteristic of tosylate displacements which occur with neighboring participation because the accumulation of positive charges in the transition state leading to **19** would be expected to inhibit the formation of a delocalized structure. Thus **1** might be expected to solvolyze to the classical ion **20**, rather than to the delocalized ion **19**. Since it is commonly accepted that *endo*-norbornyl arenesulfonates solvolyze in the



20 **1** **19**

+ $^-$OTs

rate-determining step to classical ions,[3-5,19-21] it is assumed that the *endo* tosylate (**2**) might also solvolyze to a classical ion. If the large *exo/endo* rate ratio observed in the norbornyl tosylate solvolyses is due to anchimeric assistance, **1** and **2** should solvolyze with an *exo/endo* rate ratio of approximately one since anchimeric assistance would be inhibited by the presence of the carbonyl function.

The fact that **1** solvolyzes 6.0 times slower (at 25°) than **2** appears to be most consistent with nonclassical carbonium ion theory. The factor of 6.0 is in amazingly good agreement with the calculations of Schleyer, who predicted[22] that the C-6 *endo* hydrogen, rather than slowing the rate of solvolysis of the *endo* tosylate, would actually accelerate the rate by a factor of 5 due to nonbonded interactions with the tosylate functions. However, before this conclusion can be accepted as

(15) S. Winstein, B. K. Morse, E. Grunwald, H. W. Jones, J. Corse, D. Trifan, and H. Marshall, *J. Am. Chem. Soc.*, 74, 1127 (1952); P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, 87, 375 (1965).

(16) A similar rate for the solvolysis of the *exo* tosylate has been obtained by K. Mislow and W. Meyer. For details see, W. E. Meyer, Ph.D. Thesis, New York University, 1964.

(17) For a leading reference see S. Winstein, *J. Am. Chem. Soc.*, 87, 381 (1965).

(18) For a leading reference see H. C. Brown and M. H. Rei, *ibid.*, 86, 5008 (1964).

(19) H. C. Brown, F. J. Chloupek, and M. H. Rei, *ibid.*, 86, 1248 (1964).

(20) S. Winstein and D. Trifan, *ibid.*, 74, 1147 (1952).

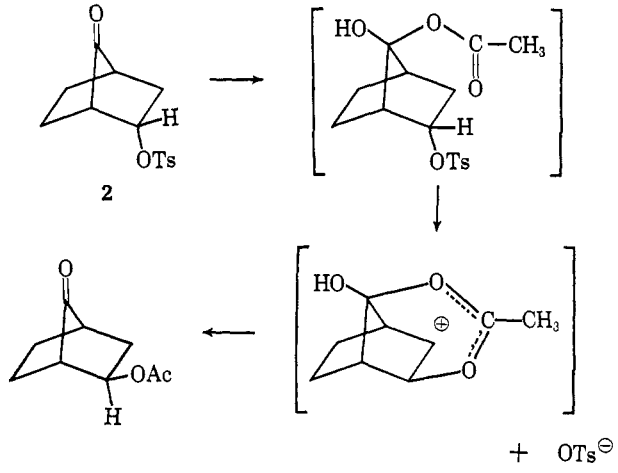
(21) P. von R. Schleyer, *ibid.*, 86, 1854 (1964).

(22) P. von R. Schleyer, Symposium on Linear Free Energy Correlations, Durham, N. C., Oct 19–21, 1964, Preprints of Papers, p 225.

being unequivocally correct, certain other possibilities must be considered. We envisage a total of three possible rationalizations of this unique *exo/endo* rate ratio: (1) the *exo* and *endo* isomers are solvolyzing by different mechanisms, (2) an unprecedented dipole–dipole interaction is occurring which either accelerates the *endo* solvolysis or inhibits the *exo* solvolysis, or (3) the *exo* tosylate **1** is solvolyzing without anchimeric assistance while all other known *exo*-norbornyl tosylates solvolyze with anchimeric assistance.

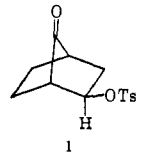
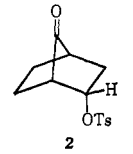
Several possibilities exist under the category of "solvolysis by different mechanisms." Two of these possibilities are plausible enough to merit discussions.

The possibility that the rate of solvolysis of **2** is accelerated by hemiketal formation, followed by an intramolecular SN2 displacement, requires consideration. Solvent interactions of this type could occur. However, if this type of internal displacement were responsible for an acceleration of the solvolysis of **2** by a factor of 10^2–10^3, changing solvent should produce a drastic change in the absolute rate of solvolysis of **2**

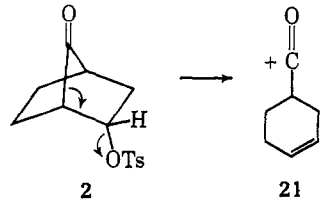


and in the *exo/endo* rate ratio. In fact, ethanolysis of **1** and **2** gave rates which were very close to the acetolysis rates both in absolute rate values (Table IV) and in the *exo/endo* rate ratio of 2.1 (at 100°) *vs.* 0.4 (at 100°) for acetolysis. It should be noted that the *exo/endo* rate ratios for both acetolysis and ethanolysis are close to unity.

Table IV. Ethanolysis Rates

Compound	Temp, °C	Rate, sec^{-1}
 1	100.00 ± 0.01	2.56×10^{-4}
	90.00 ± 0.01	$(1.21 \pm 0.01) \times 10^{-4}$
 2	100.00 ± 0.01	1.2×10^{-4}
	90.00 ± 0.01	$(4.93 \pm 0.03) \times 10^{-5}$

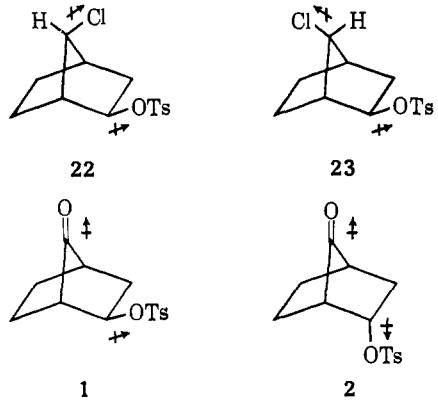
A second case of "solvolysis by different mechanisms" involves the possibility that **1** solvolyzes in a relatively straightforward manner to yield a bicyclic cation, while the solvolysis of **2** occurs *via* a concerted bond cleavage process leading to the acyl carbonium ion **21**. However,



the fact that both **1** and **2** give products with the 7-keto-norbornane skeleton intact in greater than 50% yield precludes such a concerted cleavage as the rate-determining step.

The question of dipole–dipole or dipole–ion interactions is much more complex, and as a result, much harder to resolve. It has been shown by Kwart and Takeshita[23] that not only the presence of an inductive group but also its orientation relative to the reaction site can influence solvolysis rates. The orientation factors studied by these workers generally changed the rates by a factor of less than 10. In comparing our rates with those of the epimeric norbornyl tosylates, we find a change in the *exo/endo* rate ratio of 1.7×10^3.

Additional evidence against a significant effect of dipole–dipole or dipole–ion interaction is provided by the investigation of Roberts and co-workers[24] on the solvolysis of **22** and **23**. It should be noted that the dipoles in **22** and **23** are oriented in different directions



in a manner very similar to that of **1** and **2**. It has been shown[24] that **22** solvolyzes 1.8 times faster than **23**. This clearly indicates the absence of any significant dipole effect in the solvolysis of **22** and **23**. Furthermore, if the factor of 1.8 was due to a dipole–dipole interaction, one would predict that dipole interactions would accelerate the rate of the *exo* tosylate **1** since the orientation of the *syn* isomer is comparable to the *exo* tosylate **1**. These data indicates that dipole–dipole interactions are not important in our solvolyses.

Having dismissed the possibility of **1** and **2** undergoing solvolysis *via* different mechanisms and having considered the question of dipole–dipole interactions, we conclude that, barring some *unprecedented* solvolytic mechanism, the solvolysis of **1** and **2** probably occurs in a straightforward manner. This would suggest that the rate data obtained from the solvolysis of **1** and **2** to

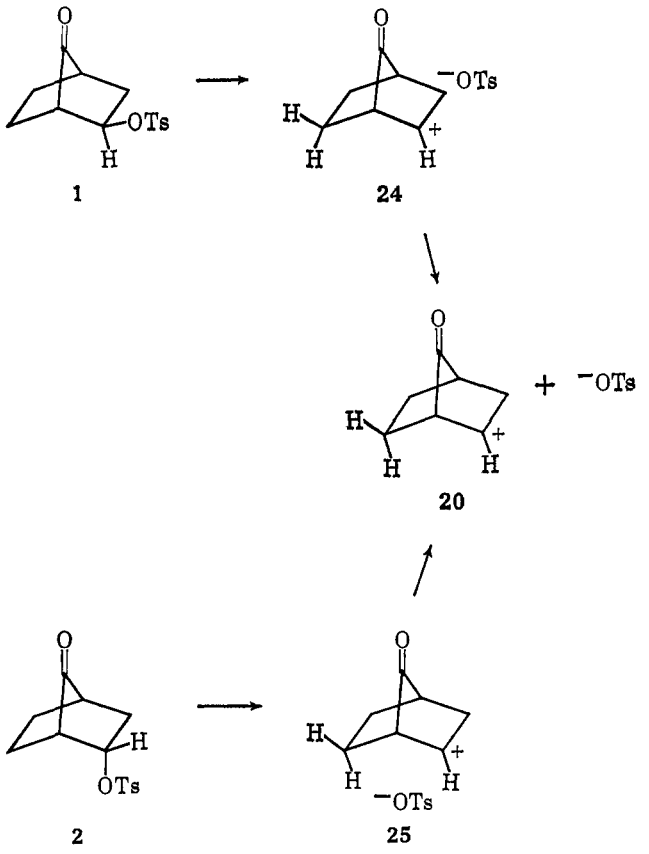
(23) H. Kwart and T. Takeshita, *J. Am. Chem. Soc.*, **86**, 1161 (1964).
(24) W. G. Woods, R. A. Carboni, and J. D. Roberts, *ibid.*, **78**, 5653 (1956).

classical carbonium ions indicates that the *endo* hydrogen at C-6 does not play a significant role in the determination of the solvolysis rate. This qualified conclusion is most consistent with nonclassical carbonium ion theory. Additional evidence that the *exo* tosylate **1** solvolyzes without anchimeric assistance while other known *exo*-norbornyl tosylates solvolyze with participation of the 1–6 σ electrons is provided by the product analysis.

Product Analysis

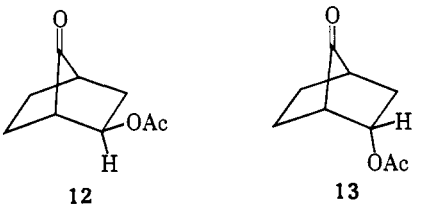
In any evaluation of the bearing of solvolytic studies on the nonclassical carbonium ion question, the stereochemistry of the solvolysis products must be considered. The overwhelming predominance of *exo* substitution, which occurs in solvolysis reactions of norbornyl tosylates, has been a topic of prime importance in discussions[5,16,25,26] of the classical *vs.* nonclassical norbornyl cation. In considering the products of solvolysis of norbornyl tosylates, Berson[5] and Winstein[17,25] have used the exclusive *exo* substitution, which occurs even in norbornyl derivatives containing *gem*-dimethyl groups in the 7 position, as evidence for the existence of a delocalized ion which shields the *endo* side of the molecule from nucleophilic addition of solvent. In contrast, Brown[26] has used the exclusive *exo* addition of solvent to certain tertiary norbornyl cations, which he presumes to be classical in nature, as a basis for questioning the use of product stereochemistry as evidence for the intermediacy of nonclassical carbonium ions in the solvolysis of bicyclo[2.2.1]heptyl tosylates.

Since **1** solvolyzes more slowly than **2**, it is probable that neither tosylate solvolyzes to yield a nonclassical carbonium ion. Thus the products resulting from the acetolyses of **1** and **2** should be those produced by the addition of acetic acid to the classical secondary carbonium ion **20**, or to the ion pairs **24** and **25**, respectively.



When the product analyses were carried out by vapor phase chromatography of the crude solvolysis mixtures, the only detectable products were 2-*endo*-acetoxybicyclo[2.2.1]heptan-7-one (**13**) and 2-*exo*-acetoxybicyclo[2.2.1]heptan-7-one (**12**). The nature of these products was established by comparison of vpc retention times on three columns and by comparison of infrared spectra of samples isolated by preparative vpc with the infrared spectra of authentic samples of **12** and **13**.

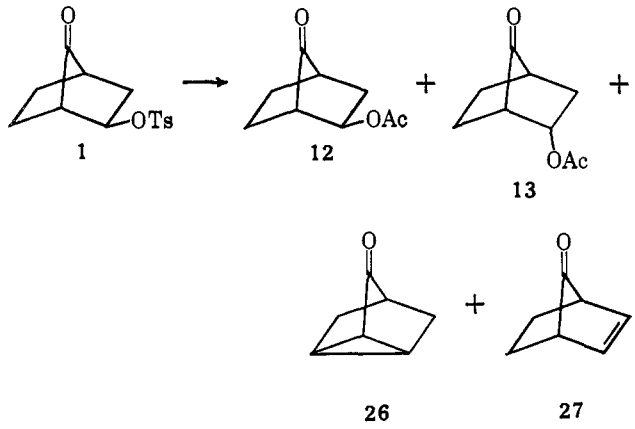
The exact yields and product ratios were very difficult to assess due to the sensitivity of **13** to heat, acid, and base. Vapor phase chromatography of the crude acetolysis mixture resulting from **1** showed only **13** and **12** in the ratio of 2:3.[14] The presence of 40% *endo*



acetate is probably a minimal value due to the thermal instability of **13**. When the acetolysis mixture was neutralized with base and the solvolysis products were isolated and distilled, a 71% yield of mixed products was obtained. This material consisted of 65% *exo* acetate and 20% *endo* acetate. Six minor components constituted the remaining 15%. The relatively low yield (71%) and reduced ratio of *endo* and *exo* products of the isolated solvolysis mixture from **1** can be attributed to the extreme sensitivity of **13** to base. It has been shown by DePuy and Story[27] that **13** "hydrolyzed completely in a few minutes at room temperature with dilute base." DePuy and Story did not characterize the products which resulted from base hydrolysis of **13**. It was felt that the minor components observed in the isolated product mixture might be a result of the reaction of **13** with base in the neutralization of the acetic acid, since these impurities were not detected in the vpc of the crude product. In order to check this postulate, a solvolysis was carried out in a minimum amount of solvent. This allowed a very rapid work-up utilizing a minimum amount of base. We found that four of the six minor components were not present under these work-up conditions. This solvolysis gave a product mixture consisting of 48% **12**, 44% **13**, 4.0% nortricyclanone (**26**), and 4.0% 7-ketonorbornene (**27**). The results of this experiment indicate that four of the minor components were resulting from the decomposition of solvolysis products during work-up.

The identification of nortricyclanone and 7-ketonorbornene as solvolysis products seemed significant. Since they have vpc retention times similar to acetic acid, they were not detected in the vpc of the total solvolysis mixture. The presence of 8% elimination products can be compared with the 4% elimination products identified in the acetolysis of *exo*-norbornyl *p*-bromobenzenesulfonate (**28**) where the nortricyclane

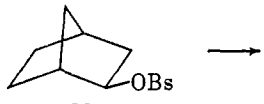
(25) S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, 74, 1147, 1154 (1952).
(26) H. C. Brown and H. M. Bell, *ibid.*, 86, 5006, 5007 (1964).
(27) C. H. DePuy and P. R. Story, *ibid.*, 82, 627 (1960).



1 12 13

26 27

to norbornene ratio was 98 to 2.[28] It was proposed that the preponderance of nortricyclane is consistent with nonclassical cation theory insofar as the intermediate that most closely resembles nortricyclane



28

would be the bridged nonclassical carbonium ion.[28] We observe a drastically different ratio in our elimination products. The ratio of 1:1 (nortricyclanone/7-ketonorbornene) indicated that a nonclassical intermediate was not formed in our solvolyses.

The major components of our solvolysis product mixture represent a drastic departure from the results observed for other norbornyl tosylates. To our knowledge this is the first case of an *exo* tosylate solvolysis in a bicyclo[2.2.1]heptyl system which yielded a large proportion of *endo* product.[29]

Analysis of the crude products from the acetolysis of **2** also showed a mixture of **12** and **13**. In this case the reaction mixture gave **13** and **12** in the ratio of 2.3:97.7.[14] Although *endo* product was observed in this solvolysis, the drastic change in product ratio, as compared to the product ratio from **1**, deserves explanation.

It appears that the products obtained from **1** and **2** are not arising from a single carbonium ion such as **20** in which the tosylate moiety is completely divorced from the carbonium ion since this would require **1** and **2** to yield identical proportions of *exo* and *endo* acetates. An attractive explanation for the observed products is that the carbonium ions formed are highly reactive since they lack the stabilization normally derived from nonclassical ion formation. As a result both **1** and **2** may be yielding products at an early stage in the separation of the ion pairs represented by **24** and **25**, respectively.

(28) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Am. Chem. Soc.*, **87**, 376 (1965).

(29) H. M. Bell and H. C. Brown, *ibid.*, **86**, 5007 (1964), report an 87:13 *exo/endo* product ratio in the reaction of sodium borohydride with 1-(*p*-anisyl)camphene hydrochloride in aqueous diglyme. However, in the absence of sodium borohydride, these same authors found no trace of *endo* products in the closely related solvolyses of either 2,7,7-trimethylnorbornyl chloride (α-fenchene hydrochloride) or *exo*-fenchyl tosylate: H. C. Brown and H. M. Bell, *ibid.*, **86**, 5006 (1964).

The ion pair **24** would be hindered on the bottom side by the *endo* hydrogen at C-6 and on the top side by the leaving tosylate ion. By comparison the ion pair **25** would have both the C-6 *endo* hydrogen and the leaving tosylate ion hindering *endo* substitution while the *exo* side would be relatively available for solvent addition.

The solvolysis results of both **1** and **2** indicate that the intermediacy of a transition state involving C_6–C_1 electron participation is insignificant in our studies. In other terms k_s (solvolysis without anchimeric assistance) is far more important than k_Δ (solvolysis with anchimeric assistance) using Winstein's terminology.[28] In relation to this, the question of the importance of direct displacement by a solvent molecule demands consideration. Direct displacement would lead to inversion.[20,30] This could explain the large amount of *exo* acetate observed in the solvolysis of **2**. We cannot rule out a certain amount of such SN2 displacement. However, the formation of *endo* acetate[20] from **2** and the formation of the observed elimination products requires that some solvolysis occurs without anchimeric assistance (k_s mechanism) and without direct displacement. This has the necessary consequence that in the solvolysis of **2** the relative amount of *endo* acetate formed from the carbonium ion resulting from ionization without anchimeric assistance (k_s) would be larger than indicated by the 97.7:2.3 ratio of *exo* to *endo* acetates since any *exo* acetate arising from direct displacement would decrease the value of 97.7%. This would be consistent with the assumption made earlier in this paper that solvolyses which occur without anchimeric assistance should yield significant amounts of *endo* products.

In view of this data, the question of why the "presumably classical"[29] tertiary norbornyl cations yield only *exo* products merits comment. If a classical secondary norbornyl cation yields both *exo* and *endo* products, it would seem that a tertiary norbornyl cation, if classical in nature, should also yield a mixture of *endo* and *exo* products. The exclusive formation of *exo* products from tertiary norbornyl cations casts doubt on the classical nature of these ions.[31] Clearly, it is necessary to give careful consideration to the question of whether the *endo* side of tertiary norbornyl cations is blocked by either a rapidly equilibrating pair of classical ions or by a delocalized "nonclassical" carbonium ion.

Experimental Section

7,7-Dimethoxybicyclo[2.2.1]heptene (4) was prepared according to the method of Gassman and Pape.[6]

7,7-Dimethoxybicyclo[2.2.1]heptane *exo*-2,3-Epoxide (5). To a solution of 0.173 mole of perbenzoic acid in 1 l. of chloroform was added 21.56 g of **4** with stirring. After standing at 5° for 7 days the reaction mixture was washed with two 125-ml portions of 10% sodium hydroxide and two 150-ml portions of water. The organic layer was dried over anhydrous magnesium sulfate and filtered; the solvent removed under reduced pressure. The residue was fractionally distilled to yield 20.92 g (87%)[32] of **5**, bp 53–56° (0.4 mm). Redistillation gave an analytical sample, $n^{25}D$ 1.4738.

Anal. Calcd for $C_9H_{14}O_2$: C, 63.51; H, 8.29. Found: C, 63.45; H, 8.37.

(30) S. J. Cristol and G. D. Brindell, *ibid.*, **76**, 5699 (1954).

(31) S. Winstein, *ibid.*, **87**, 381 (1965), also discusses the possibility that evidence seems "to favor preferred bridged structures for typical secondary and tertiary norbornyl cations."

(32) An identical yield may be obtained by using the more convenient reagent *m*-chloroperbenzoic acid (FMC Corp.).

7,7-Dimethoxybicyclo[2.2.1]heptan-*exo*-2-ol (6). To a slurry of 18.28 g of lithium aluminum hydride in 600 ml of dry tetrahydrofuran was added dropwise 22.76 g of **5**. The reaction mixture was stirred under reflux for 12 days. The tetrahydrofuran solution was cooled to 0° and 70 ml of water was added dropwise with vigorous stirring. The reaction mixture was then stirred at room temperature for 2 hr, filtered, and concentrated under reduced pressure. The remaining liquid was fractionally distilled to yield 21.70 g (94%) of pure *exo* alcohol,[33] **6**, bp 62–72° (0.6 mm). Redistillation gave an analytical sample, bp 50.5–51.0° (0.35 mm), n^{27}D 1.4676.

Anal. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.76; H, 9.43.

***exo*-2-Hydroxybicyclo[2.2.1]heptan-7-one (3).** A mixture of 0.68 g of **6** and 5 ml of 5% sulfuric acid was stirred vigorously for 16 hr. The resulting emulsion was extracted with three 10-ml portions of ether. The combined extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated under vacuum to give 0.39 g (78%) of a yellow-tinted oil. Attempted distillation of a sample of this material resulted in considerable decomposition. Sublimation and preparative vapor phase chromatography also gave decomposition. Due to the difficulties in purification, a satisfactory elemental analysis was not obtained.

***exo*-2-Acetoxybicyclo[2.2.1]heptan-7-one (12).** Freshly prepared **3** from 1.30 g of **6** was dissolved in 10 ml of pyridine. To this solution with swirling was added 1.0 g of acetyl chloride dropwise. After the mixture stood at 0° overnight, it was poured over 50 ml of water and extracted with four 20-ml portions of ether. The combined extracts were dried over anhydrous magnesium sulfate, concentrated under reduced pressure, and distilled to yield 0.29 g (23% over-all) of **12**, bp 59–62° (0.20 mm). The nmr chemical shift of the proton α to the acetate function was positioned at τ 5.18. Preparative vpc (15% didecyl phthalate on Chromosorb P) enabled an analytical sample to be isolated, bp 65° (0.03 mm), $n^{25.0}$D 1.4690.

Anal. Calcd for $C_9H_{12}O_3$: C, 64.27; H, 7.19. Found: C, 64.02; H. 7.32.

Reduction of 12 with Lithium Aluminum Hydride. A mixture of 20 mg of **12** and 20 mg of lithium aluminum hydride in 20 ml of dry ether was stirred at room temperature for 4 hr. The product was worked up and isolated in the usual manner to yield *exo*-2-*syn*-7-norbornanediol (**14**) identical with an authentic sample.

Preparation of 12 by the Hydrolysis of 9. A mixture of the ketal acetate **9** (3.99 g) in 20 ml of 5% sulfuric acid was stirred vigorously for 6 hr, followed by extraction with four 10-ml portions of ether. To the combined extracts was added 4 ml of pyridine. The extracts were dried with anhydrous magnesium sulfate, concentrated under vacuum, and distilled to yield 0.94 g of *exo*-2-acetoxybicyclo[2.2.1]-heptan-7-one, bp 55° (0.02 mm), with a small amount of the further hydrolyzed product **3**. Continuous extraction of the aqueous phase gave an additional 1.59 g of the keto acetate for a cumulative yield of 81%.

***exo*-2-Hydroxybicyclo[2.2.1]heptan-7-one *p*-Toluenesulfonate (1).** A sample of freshly prepared **3** from 1.93 g of **6** was converted to its tosylate according to the procedure of Tipson.[13] After standing for 21 hr at 0°, the purple solution was poured over 50 ml of water and was extracted with four 15-ml portions of chloroform. The combined extracts were washed with two 10-ml portions of 20% aqueous sulfuric acid and then with two 10-ml portions of water, dried with anhydrous magnesium sulfate, and concentrated to a pink syrup. Recrystallization from ether–hexane gave 1.13 g (36% over-all) of the tosylate, mp 72.4–73.0°. The nmr chemical shift of the α proton was centered at τ 5.27.

Anal. Calcd for $C_{14}H_{16}O_4S$: C, 59.98; H, 5.75; S, 11.44. Found: C, 60.04; H, 5.70; S, 11.40.

***endo*-2-Hydroxybicyclo[2.2.1]heptan-7-one (11).** A mixture of 1.16 g of **7** and 8 ml of 5% sulfuric acid was stirred vigorously for 23 hr. The resulting solution was extracted with six 10-ml portions of ether. The combined extracts were dried with anhydrous potassium carbonate and magnesium sulfate and were concentrated under reduced pressure to yield 0.66 g (78%) of a clear syrup which could not be obtained pure due to rapid decomposition.

***endo*-2-Acetoxybicyclo[2.2.1]heptan-7-one (13).** Freshly prepared **11** from 0.63 g of **7** was dissolved in 8 ml of pyridine. To the solution with swirling was added dropwise 0.62 g of acetyl chloride. After standing at 0° for 14 hr, the pink solution was poured over 50 ml of water and extracted with three 25-ml portions of ether. The combined extracts were washed with 10 ml of water, dried over anhydrous magnesium sulfate, concentrated under reduced pressure, and distilled to yield 0.26 g of a clear oil (31%), bp 80° (1 mm).[34] The nmr chemical shift of the α proton was positioned at τ 4.86.

***endo*-2-Hydroxybicyclo[2.2.1]heptan-7-one *p*-Toluenesulfonate (2).** Freshly prepared **11** from 3.42 g of **7** was dissolved in 23 ml of pyridine. To this solution at 0° was added with stirring 4.50 g of *p*-toluenesulfonyl chloride. The resulting solution was allowed to stand at 0° for 65 hr. The purple reaction mixture was poured over 750 ml of water and extracted with three 100-ml portions of chloroform. The combined extracts were concentrated under reduced pressure to a purple syrup and chromatographed through silica gel with 10% ether in benzene to give 2.63 g (47% over-all) of an alcohol-free clear oil.[35] The nmr chemical shift of the α proton was centered at τ 5.02.

Hydroboration[10] of 4. Diborane, generated by the dropwise addition of 3.9 g of sodium borohydride (103 mmoles) in 100 ml of diglyme to 53.1 g of 47% boron trifluoride etherate (145 mmoles) in 100 ml of diglyme over a period of 3 hr, was passed through a solution of 10.1 g (66 mmoles) of **3** in 150 ml of dry tetrahydrofuran at 0°. To the latter solution was added 10 g of sodium hydroxide in 55 ml of water and 35 ml of 30% hydrogen peroxide. After 1 hr of stirring, the resulting two phases were separated and the aqueous phase was extracted with 50 ml of ether. The organic phases were combined and diluted with 150 ml of ether. The resulting aqueous layer was drawn off, and the ether phase was washed with 50 ml of water, dried with anhydrous magnesium sulfate, concentrated under vacuum, and distilled to yield 8.76 g, bp 60–93° (1.3 mm), of a clear oil which consisted of 75% of the *exo* alcohol **6**, 20% of the *endo* alcohol **7**, and 5% of an unidentified component, resulting in a 74% over-all yield for **6** and **7** combined.

Reduction of 5 with Lithium Ethylamine. To a solution of 2.63 g of **5** in 47 ml of anhydrous ethylamine at 0° was added with stirring 1.0 g of lithium in small pieces over a duration of 10 min. After 45 min the reaction mixture was quenched with 100 ml of water and extracted with four 100-ml portions of methylene chloride. The combined extracts were washed with two 50-ml portions of water, dried over anhydrous magnesium sulfate, concentrated under vacuum, and distilled to yield 0.63 g (24%) of **6**, bp 53–62° (0.5 mm). Sublimation of the pot residue gave 0.30 g (15%) of *exo*-2-*syn*-7-bicyclo[2.2.1]heptanediol (**14**), mp 178.0–178.5°. The infrared spectrum was identical with that of an authentic sample, and the mixture melting point was undepressed.

7,7-Dimethoxybicyclo[2.2.1]heptan-2-one (15). To 170 ml of pyridine at 0° was added with stirring 14.4 g of chromium trioxide. When the pyridine–chromium trioxide complex was formed, 4.98 g of **6** was added. The reaction mixture was stirred for 15 hr, poured into 1 l. of water, and continuously extracted with ether, which was subsequently dried over anhydrous magnesium sulfate. The ethereal solution was filtered and concentrated under vacuum to give an oil which on distillation yielded 4.10 g (83%) of **15**, bp 52–56° (0.2 mm). Redistillation gave a pure product, n^{32}D 1.4660, which crystallized when cooled. Recrystallization from 35–45° petroleum ether and sublimation yielded an analytical sample, mp 33–35°.

Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.37; H, 8.32.

2,4-Dinitrophenylhydrazone of 15. A sample of **15** (0.11 g) in 3 ml of 0.25 *M* 2,4-dinitrophenylhydrazine in phosphoric acid and ethanol immediately yielded a precipitate. After standing in the reagent for 8 hr, the crystals were collected and recrystallized from 95% ethanol four times and eluted through grade IV Woelm alumina with benzene to give an analytical sample as fine yellow needles, mp 208.5–209.0°.

Anal. Calcd for $C_{15}H_{18}N_4O_6$: C, 51.42; H, 5.18; N, 15.99. Found: C, 51.23; H, 5.21; N, 16.04.

7,7-Dimethoxybicyclo[2.2.1]heptan-*endo*-2-ol (7).[36] A 500-ml three-necked flask fitted with a short Vigreux column and a dropping funnel was filled with 11.96 g of ketone **15**, 18.6 g of crushed aluminum isopropoxide, and 600 ml of isopropyl alcohol. This

(33) All analyses for the purity of the epimeric alcohols, **6** and **7**, were by vapor phase chromatography on Carbowax 20M on Chromosorb W.

(34) C. H. DePuy and P. R. Story, *J. Am. Chem. Soc.*, **82**, 627 (1960), report bp 57° (0.5 mm) for **13**.

(35) Due to the extreme difficulty encountered in rigorously purifying this compound, a satisfactory elemental analysis could not be obtained. Titrimetric data indicated a purity of 88.9% on the material used in the rate measurements.

(36) Meerwein–Ponndorf–Verley reduction: A. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., London, 1956, pp 882–886.

mixture was distilled slowly until no acetone could be detected in the distillate (5 hr). The mixture was then concentrated under vacuum to yield a residue which was dissolved in 1100 ml of 5% sodium hydroxide solution. This solution was extracted with five 250-ml portions of ether; the ether extracts were combined, dried with anhydrous magnesium sulfate, concentrated under vacuum, and distilled to yield 10.95 g (91%) of the *endo* alcohol **7**, bp 75–79° (1.0 mm), of which the *exo* epimer **6** comprised 2%. Redistillation of this viscous product gave an analytical sample, bp 77° (0.28 mm), $n^{29}D$ 1.4767.

Anal. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.63; H, 9.40.

It was discovered that the rate at which the solvent was distilled off was critically important. When the solvent was distilled at a slow rate, considerable amounts of the *exo* epimer **6** resulted. The amount of **6** was held to a minimum when the solvent was removed rapidly (2–3 ml/min).

Reduction of 15 with Lithium Aluminum Hydride. To a stirring slurry of 0.32 of lithium aluminum hydride in 5 ml of dry ether at 0° was added 0.32 g of the ketone **15** in 5 ml of dry ether. After 2 hr of stirring, 2 ml of water was added dropwise. After 45 min of subsequent stirring, filtration and concentration under vacuum gave 0.25 g (77%) of an oily residue which consisted of a 3:1 ratio of the *exo* alcohol **6** to the *endo* alcohol 7.

Reduction of 15 with Sodium–Ethanol. Sodium–ethanol reduction of the ketone **15** was always incomplete, even with a large excess of sodium. A typical run consisted of adding 11.0 g of sodium in small pieces to a stirring solution of 2.22 g of the ketone **15** in 100 ml of absolute ethanol over a period of 5 hr. This solution was poured over 1 l. of ice water and extracted with three 300-ml portions of ether. The extracts were combined, washed with 50 ml of water, dried with anhydrous magnesium sulfate, concentrated under vacuum, and distilled to yield 1.27 g of a clear liquid, bp 70–73° (0.6 mm), which consisted of 16% of the *endo* alcohol **7**, 38% of the *exo* alcohol **6**, and 46% of unreacted ketone **15**.

Oxidation of the *endo* Alcohol 7. Addition of 0.27 g of **7** to a mixture of 0.87 g of chromium trioxide in 5 ml of pyridine gave, after dilution with 75 ml of water, extraction with three 25-ml portions of ether, drying with anhydrous magnesium sulfate, and concentration under vacuum, an oil which proved by vapor phase chromatography to consist exclusively of pyridine and the ketone **15**. The infrared spectrum of the ketone collected by preparative vapor phase chromatography was identical with that of **15**.

***exo*-2-Acetoxy-7,7-dimethoxybicyclo[2.2.1]heptane (9).** To a solution of 4.30 g of **6** in 40 ml of pyridine was added dropwise 2.8 g of acetyl chloride with swirling. After standing for 15 min, the resulting mixture was poured over 400 ml of water and extracted with four 50-ml portions of ether. The combined extracts were dried over anhydrous magnesium sulfate and concentrated under vacuum to yield a yellow oil which on fractional distillation gave 4.76 g (89%) of the acetate **9**, bp 83–85° (0.6 mm). Redistillation gave an analytical sample, bp 104–105° (6 mm), $n^{26}D$ 1.4587.

Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.51; H, 8.50.

***endo*-2-Acetoxy-7,7-dimethoxybicyclo[2.2.1]heptane (10).** Treatment of **7** as above gave an 89% yield (1.66 g) of the *endo* acetate, which crystallized when cooled. An analytical sample was prepared by redistillation, bp 67° (0.3 mm). A sample recrystallized from hexane gave white flakes, mp 29.0–30.1°.

Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.39; H, 8.49.

Kinetics. Anhydrous acetic acid was prepared by refluxing a solution of acetic anhydride and sodium acetate in glacial acetic acid for 24 hr with subsequent distillation in a dry atmosphere. Standard sodium acetate solution was prepared by the careful addition of acetic acid to a solution of sodium carbonate in acetic anhydride. Acetolyses were conducted in the usual manner,[37] using bromophenol blue in dry acetic acid as the indicator. The acetolyses of **1** and **2** were carried out over 1.6 and 3.0 half-lives, respectively, during which pseudo-first-order kinetics were excellent.

Acetolysis Product Analysis of 1.[38] A solution of 2.431 g of **1** and 0.742 g of anhydrous sodium acetate in 59 ml of acetic acid containing 5 drops of acetic anhydride was heated on a steam bath for 11.5 hr. The solution was then cooled and mixed with 300 ml of water. To the stirring mixture was added in portions 70 g of sodium bicarbonate. The resulting mixture was extracted with six 100-ml portions of ether and the combined ethereal extracts were dried over anhydrous magnesium sulfate, concentrated under reduced pressure, and distilled to yield 1.037 g (71%) of a yellow oil, bp 55–70° (0.2 mm). Vapor phase chromatography indicated a composition of 65% *exo* acetate (**12**), 20% *endo* acetate (**13**), and 15% of six other unidentified components. Preparative vapor phase chromatography of the distilled acetolysis product mixture (30% Carbowax 20M on 42–60 firebrick) allowed the isolation of pure samples of **12** and **13** which were shown to be identical with authentic samples by infrared spectroscopy. Additional confirmation of the assigned structures of the acetolysis products was available by comparing retention times of the acetolysis products with those of authentic samples of **12** and **13** on 15% butanediol succinate on firebrick no. 20.

Vapor phase chromatography of crude acetolysis mixtures in two separate runs indicated the presence of only **12** and **13** in a respective composition[14] of 60 and 40%.

An independent experiment established that **12** did not epimerize to **13** (±0.1%) under acetolysis conditions.

A solution of 0.035 g of **1** in 0.50 ml of anhydrous acetic acid buffered with 0.1 *M* sodium acetate was heated at 100.00° for 646 min, cooled, mixed with 50 ml of water, and quickly neutralized with sodium bicarbonate. The resulting solution was immediately extracted with 100 ml of ether. The etheral extract was dried with anhydrous magnesium sulfate and concentrated under reduced pressure. Vapor phase chromatography indicated the presence of only **12, 13, 26,** and **27** in the respective ratio of 48:44:4.0:4.0. Each of the products was shown independently not to convert to any other compounds under identical acetolysis conditions.

Acetolysis Product Analysis of 2. A solution of 1.437 g of alcohol-free **2** (88.9% pure as determined by titration after complete acetolysis) and 0.445 g of anhydrous sodium acetate in 50 ml of acetic acid containing 5 drops of acetic anhydride was heated on a steam bath for 4.5 hr. This mixture was worked up and distilled in a manner identical with that used for **1** to yield 425 mg (59%, calculated on 88.9% original tosylate) of a yellow oil. Vapor phase chromatography indicated a composition of 76% *exo* acetate (**12**), 3% *endo* acetate (**13**), and 21% of unidentified components.

A sample of alcohol-free **2** was solvolyzed under identical conditions. Vapor phase chromatography of the crude acetolysis mixture indicated only the products **12** and **13** in a respective composition[14] of 97.7 and 2.3%.

The original sample of **2** was rechromatographed on silica gel to remove any possibly remaining traces of **1** or **11**. Vapor phase chromatography of the crude acetolysis mixture of this sample of **2** gave the respective percentages[14] of **12** and **13** as 97.8 and 2.2%. The chromatography of the *endo* tosylate was shown to completely remove any traces of *endo* alcohol **11** or the *exo* tosylate **1**, which might have been responsible for the formation of the *endo* acetate **13**.

Ethanolysis Procedure. Pure ethanol was prepared by the procedure of Fieser.[39] Kinetic measurements were carried out in the manner of Winstein,[37] using standardized sodium methoxide in methanol as a titration base and 0.1% alcoholic bromophenol blue as the indicator.[40] The ethanolysis of **1** gave good kinetics throughout 2 half-lives, but that of **2** gave a rate which continually increased. Therefore, an initial rate for **2** is included, which is calculated for 0.2 half-life wherein the rate curve was linear.

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(38) All glpc analyses were determined on 15% Carbowax 20M on Chromsorb W unless otherwise designated.

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(40) A. M. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956).