The Solvolytic Behavior of the Four Epimeric 7-Chloro-2-hydroxybicyclo[2.2.1]heptane *p*-Toluenesulfonates[1]

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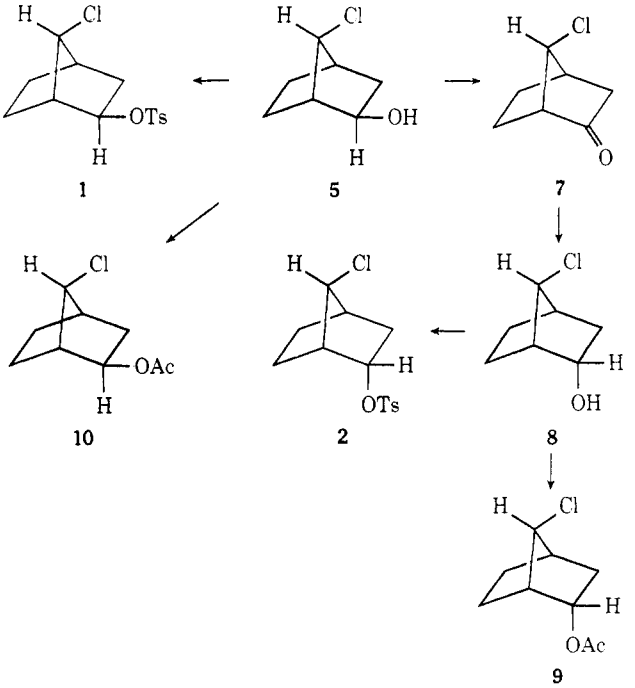
Abstract: The four epimeric 7-chloro-2-hydroxybicyclo[2.2.1]heptane *p*-toluenesulfonates have been prepared and their solvolytic behavior has been studied in buffered acetic acid. The *syn*- and *anti*-7-chloro-*exo*-2-hydroxybicyclo[2.2.1]heptane *p*-toluenesulfonates differed by less than a factor of two in rate of solvolysis. Similarly, the two epimeric 7-chloro-*endo*-2-hydroxybicyclo[2.2.1]heptane *p*-toluenesulfonates solvolyzed at rates which differed by only a factor of two. However, the exo/endo rate ratios for the two anti epimers and the two syn epimers were 80 and 246, respectively. Kinetically, these ratios parallel that of the parent norbornyl system. All four epimeric tosylates gave the same products. The product mixtures obtained from the two *anti*-chloro tosylates were identical within the limits of detection by vpc. The product mixtures obtained from the two *syn*-chloro tosylates differed considerably in per cent composition. The implications of these results in relation to norbornyl cation theory are discussed.

Both carbonium ion stabilizing[3] and carbonium ion destabilizing groups[4] have been widely used in attempts to elucidate the nature of various perplexing cations such as those which are so often associated with bicyclic ring systems. Unfortunately, many of the electron-withdrawing substituents which have been studied contain oxygen atoms which can cause unprecedented complications due to neighboring group participation.[4c-e] This participation can vary in character from direct stabilization of the incipient carbonium ion by the nonbonding electrons on oxygen[4c] to participation of carbonyl groups *via* their enols.[4e] In the hope of avoiding some of the complications inherent in the use of oxygenated functions, we decided to determine the effect of utilizing chlorine as an electron-withdrawing substituent in the destabilization of incipient carbonium ions. It was with this objective in mind that we undertook the investigation of the solvolytic behavior of the four epimeric 7-chloro-2-tosyloxybicyclo[2.2.1]heptanes (**1**–**4**),[5,6] on which we now wish to report in detail.

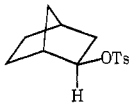
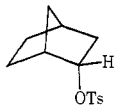
Synthesis and Solvolysis

Both *syn*-7-chloro-*exo*-2-hydroxybicyclo[2.2.1]heptane (**5**) and *anti*-7-chloro-*exo*-2-hydroxybicyclo[2.2.1]-heptane (**6**), and their corresponding tosylates **1** and **3**, respectively, were prepared according to the procedure of Roberts and coworkers.[7] Oxidation of **5** with Jones reagent gave *syn*-7-chlorobicyclo[2.2.1]heptan-2-one (**7**).[9-11] Meerwein–Ponndorf–Verley reduction of **7** gave a 95:5 mixture of **8** and **5**, respectively. Chromatography on silica gel gave pure **8**, which eluted after **5**. Reaction of **8** with tosyl chloride and with acetyl



(1) For a preliminary communication of part of this work, see P. G. Gassman and J. M. Hornback, *J. Amer. Chem. Soc.*, **91**, 4280 (1969).
(2) National Science Foundation Trainee, 1965–1968.
(3) H. C. Brown and M.-H. Rei, *J. Amer. Chem. Soc.*, **86**, 5004 (1964); H. C. Brown and K. Takeuchi, *ibid.*, **90**, 5268 (1968); H. C. Brown, F. J. Chloupek, and M.-H. Rei, *ibid.*, **86**, 1248 (1964); P. G. Gassman and A. F. Fentiman, Jr., *ibid.*, **92**, 2549 (1970).
(4) (a) P. G. Gassman and J. L. Marshall, *ibid.*, **88**, 2822 (1966); (b) P. G. Gassman and J. L. Marshall, *Tetrahedron Lett.*, 2429, 2433 (1968); (c) P. G. Gassman and J. G. Macmillan, *J. Amer. Chem. Soc.*, **91**, 5527 (1969); (d) P. G. Gassman and J. M. Hornback, *ibid.*, **91**, 5817 (1969); (e) P.G. Gassman, J. L. Marshall, and J. M. Hornback, *ibid.*, **91**, 5811 (1969); (f) J. W. Wilt and W. J. Wagner, *ibid.*, **90**, 6135 (1968); (g) R. Muneyuki and T. Yano, *ibid.*, **92**, 746 (1970).
(5) *syn*-7-Chloro-*exo*-2-tosyloxybicyclo[2.2.1]heptane (**1**) and *anti*-7-chloro-*exo*-2-tosyloxybicyclo[2.2.1]heptane (**3**) have been previously studied.[7] However, these studies only provided rate data on the *exo*-tosylates and product studies were based on infrared comparisons of reaction mixtures.
(6) Subsequent to the publication of our preliminary report on this investigation[1] a somewhat detailed study of the solvolytic behavior of **1** and **3** appeared[8] in which the problems associated with internal return were discussed.
(7) W. G. Woods, R. A. Carboni, and J. D. Roberts, *J. Amer. Chem. Soc.*, **78**, 5653 (1956); J. D. Roberts, F. O. Johnson, and R. A. Carboni, *ibid.*, **76**, 5692 (1954).
(8) H. L. Goering and M. J. Degani, *ibid.*, **91**, 4506 (1969).
(9) Roberts and coworkers[7] had previously prepared **7** and **11** by nitric acid oxidation of **5** and **6**, respectively.
(10) R. R. Sauers and J. A. Beisler, *J. Org. Chem.*, **29**, 210 (1964); J. Meinwald, C. B. Jensen, A. Lewis, and C. Swithenbank, *ibid.*, **29**, 3469 (1964).
(11) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

Table I. Solvolysis Rates of 7-Chloro-2-tosyloxynorbornanes in Acetic Acid Buffered with Sodium Acetate

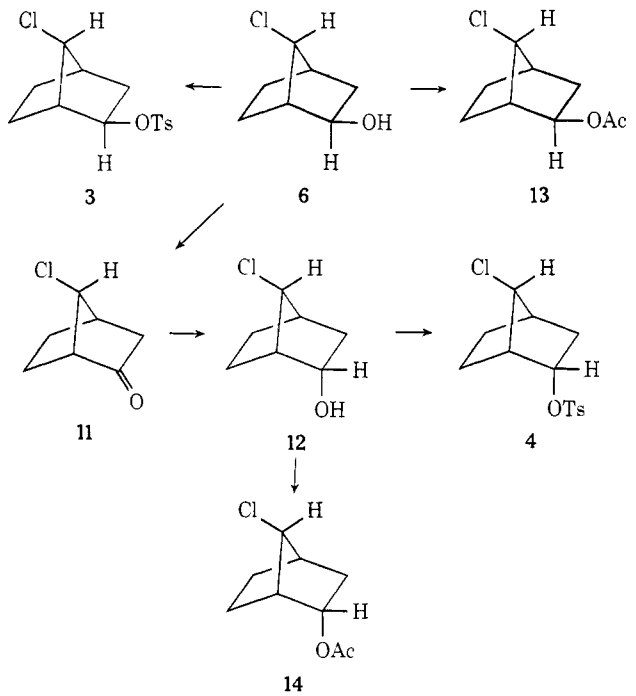
Compound	Temp, °C	Rate, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{rel}, 25°
1	100.0 ± 0.02	$(6.68 \pm 0.08) \times 10^{-4}$			
	90.0 ± 0.02	$(1.99 \pm 0.01) \times 10^{-4}$	26.4	−2.9	
	80.0 ± 0.02	$(8.37 \pm 0.04) \times 10^{-5}$			
	(25)[a]	6.62×10^{-8}			246
	78.2[b]	6.6×10^{-5}			
2	130.0 ± 0.02	$(1.24 \pm 0.02) \times 10^{-4}$			
	120.0 ± 0.02	$(5.04 \pm 0.03) \times 10^{-5}$	29.1	−4.7	
	110.0 ± 0.02	$(1.77 \pm 0.01) \times 10^{-5}$			
	(25)[a]	2.69×10^{-10}			1
3	100.0 ± 0.02	$(5.40 \pm 0.04) \times 10^{-4}$			
	90.0 ± 0.02	$(1.73 \pm 0.00) \times 10^{-4}$	26.9	−2.0	
	80.0 ± 0.02	$(6.58 \pm 0.03) \times 10^{-5}$			
	(25)[a]	4.29×10^{-8}			160
	78.2[b]	5.2×10^{-5}			
4	130.0 ± 0.02	$(2.71 \pm 0.03) \times 10^{-4}$			
	120.0 ± 0.02	$(1.08 \pm 0.01) \times 10^{-4}$	29.3	−2.7	
	110.0 ± 0.02	$(3.81 \pm 0.00) \times 10^{-5}$			
	(25)[a]	5.38×10^{-10}			2
 **15**	(25)[c]	2.33×10^{-5}			85,000
 **16**	(25)[c]	8.28×10^{-8}			310

[a] Extrapolated from higher temperatures. [b] See ref 7 and 8. [c] P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *J. Amer. Chem. Soc.*, **87**, 375 (1965).

chloride gave **2** and **9**, respectively, while reaction of **5** with acetyl chloride produced **10**.

In a parallel set of transformations, the anti epimer **6** was converted into **11** by Jones oxidation.[9-11] Lithium aluminum hydride reduction of **11** gave a 9:1 mixture of **12** and **6**, respectively. Reaction of **6** and **12** with acetyl chloride gave **13** and **14**, respectively, while reaction of **12** with tosyl chloride produced **4**.

The rates of solvolysis of compounds **1–4** in acetic acid buffered with sodium acetate are listed in Table I. The rates of solvolysis of *exo*-norbornyl tosylate (**15**) and *endo*-norbornyl tosylate (**16**) are included in this table for comparison purposes. As shown in Table I the exo/endo rate ratio for the epimeric pair **1** and **2** was 246,[12] while the similar ratio for the pair **3** and **4** was 80. It is important to note that the exo/endo rate ratios for these epimeric pairs of chloro tosylates remain high, and comparable in size to that of the parent epimeric norbornyl tosylates (exo/endo rate ratio of 281) in spite of the presence of the electron-withdrawing chloro group. It is clear from the data that the inductive effect of the chloro group in the 7 position of the four epimeric chloro tosylates is responsible for a rate decrease of approximately 300 relative to **15** and **16**. This overall rate deceleration is roughly what would be predicted on the basis of the electron-withdrawing ability of chlorine.



Careful analysis of the product mixtures obtained in the solvolyses of **1–4** provided the information listed in Table II. Since our product analyses were carried out after 10% reaction,[13] we have included in the table the

(12) The ratio for the *syn*-7-chloro pair, **1** and **2**, will be very slightly influenced by the effect of the internal return of **1** to **3** discussed by Goering and Degani.[8] However, since the amount of this internal return is small, and since the rates of **1** and **3** differ only *ca.* 20%, the exo/endo rate factor should be good to within 5%. The direction of this correction factor would indicate a maximum reduction in the exo/endo rate factor from 246 to 234.

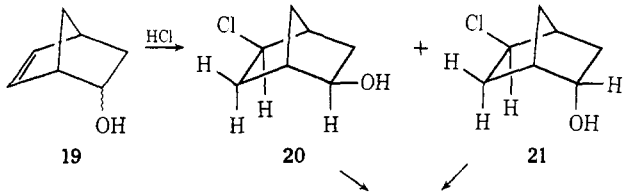
(13) Product analyses were carried out after *ca.* 10% reaction since considerable decomposition (darkening) of the solvolysis mixture occurred on prolonged reaction time. Since Goering and Degani reported product composition after 10 half-lives (*ca.* 50 times the reaction period of our analysis), it was surprising that the values for the product ratio of the mixture obtained from **3** were in such good agreement. This indicated that the observed coloration was not due to the selective decomposition of either **10** or **13**.

Table II. Products from the Acetolysis of 7-Chloro-2-tosyloxybicyclo[2.2.1]heptane after 10% Reaction

Starting tosylate	Percentage composition of the product mixture				
	10	**13**	**17**	**18**	Other
1[c]	45	42	9	2	2
	33[a]	49[a]			(17)[a,b]
2	24	42	8	16	9
3[c]	14	70	9	4	3
	14[a]	71[a]			(15)[a,b]
4	11	69	8	7	5

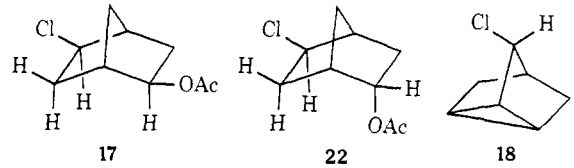
[a] Percentage after 10 half-lives.[8] [b] These products were not identified, but it was noted that there were three components which made up this percentage.[8] [c] Roberts and coworkers previously reported[7] a product study on both **1** and **3** in which they estimated, on the basis of infrared analysis, that both **1** and **3** gave a 50:50 mixture of **10** and **13**.

product analyses on **1** and **3** reported by Goering and Degani.[8] The products were identified by comparison with authentic samples. An authentic sample of *exo*-2-chloro-*exo*-5-acetoxybicyclo[2.2.1]heptane (**17**) was prepared by the addition of gaseous hydrogen chloride to 5-hydroxybicyclo[2.2.1]heptene (**19**) which gave a 1:2 mixture[14] of **20** and its endo isomer **21**. The epimeric nature of **20** and **21** was demonstrated by the oxidation of both **20** and **21** to **22**. The predominance of **21** in the mixture from hydrogen chloride addition



19 **20** **21** **22**

was not desirable. This situation was remedied by Meerwein–Ponndorf–Verley equilibration of this reaction mixture, which changed the exo/endo product ratio from 1:2 to 2:1. The increase in the proportion of **20** under these conditions supported the assignment of the exo stereochemistry to the hydroxyl group of **20**. Reaction of this mixture with acetic anhydride in pyridine gave a mixture of **17** and **22**, which was separated



17 **22** **18**

by preparative vpc. The other minor product, **18**, was identified through comparison with an authentic sample of **18** prepared according to the procedure of Roberts and coworkers.[16]

(14) A related addition of nitric acid to **19** gave a mixture of *exo*-5-nitro-*exo*-2-hydroxybicyclo[2.2.1]heptane and *exo*-5-nitro-*endo*-2-hydroxybicyclo[2.2.1]heptane in which the endo hydroxy epimer predominated.[15]

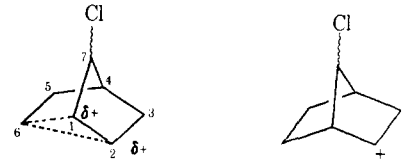
(15) H. Toivonen, *Soum. Kemistilehti B*, **31**, 354 (1958).

(16) J. D. Roberts, F. O. Johnson, and R. A. Carboni, *J. Amer. Chem. Soc.*, **76**, 5692 (1954).

Considerable effort was expended in attempting to determine whether either of the two isomeric 7-chloro-*endo*-2-acetoxybicyclo[2.2.1]heptanes was generated in the solvolysis of **1**–**4**. However, within the limits of detection by vpc analysis, we found no trace of either *syn*-7-chloro-*endo*-2-acetoxybicyclo[2.2.1]heptane (**9**) or *anti*-7-chloro-*endo*-2-acetoxybicyclo[2.2.1]heptane (**14**).[17]

Discussion

The rate factors listed in Table I show that the inductive effect of the 7-chloro group influences the rate of solvolysis of both the exo and endo tosylates to approximately the same extent. Both the exo and endo isomers solvolyze approximately 300 times slower than the corresponding norbornyl tosylates, with the net result that the two epimeric exo–endo pairs, **1** and **2** and **3** and **4**, have exo/endo rate ratios similar to that of **15** and **16**. Since inductive effects decrease as the distance from the reactive center is increased, the similar rate retarding effect of the β-chloro substituents on both the exo and endo tosylate solvolysis is significant. If the transition state for the solvolysis of the exo isomer involves neighboring group participation, which leads to a delocalized ion such as **23**, there will be some



23 **24**

buildup of positive character at C-1 in the rate-determining step. By comparison, it should be noted that the solvolysis of endo tosylates to initially yield classical cations such as **24** is a generally accepted concept. Thus, the fact that the 7-chloro substituent has little effect on the exo/endo rate ratio, in our examples, implies that the distance from the electron-withdrawing substituent to the developing centers of positive charge must be comparable for both the exo and endo tosylates. This would indicate that if the transition state leading to the cation generated from the endo tosylate involves no charge delocalization to C-1, the transition state leading to the cation generated from the exo isomer must also have little, if any, charge buildup at C-1. If this were not true the 7-chloro group should inductively slow the ionization of the exo tosylate considerably more than it slows the ionization of the endo tosylate.[18] Thus, the kinetic data would tend to support the contention that neighboring group participa-

(17) Several extremely minor products were present in the mixture of products obtained in the acetolysis of **1**–**4**. These are collectively listed under the heading "other" in Table II with the percentages being calculated on the assumption that the vpc response of these components would be similar to those of **10**, **13**, **17**, and **18**. Two very minor components (*ca.* 0.5% each) had retention times similar to **9** and **14** on several vpc columns, but on other columns no peaks were detected from the product mixture which could correspond to either **9** or **14**.

(18) It is interesting to note that Goering and Degani have suggested[8] that the exo tosylates **1** and **3** are accelerated about as much as *exo*-norbornyl tosylate (**15**) based on correlation with carbonyl stretching frequencies, using the Foote–Schleyer type[19] of correlation. However, Schleyer and coworkers have recently presented data which raise serious questions about the applicability of the Foote–Schleyer correlation.[20] While we feel that the correlation of solvolysis rates with carbonyl stretching frequencies is a reasonable process when simple cyclic systems are involved, we place little faith in the value of the predications of such a correlation when unusual steric effects are involved or when unusual substituent inductive effects are present.

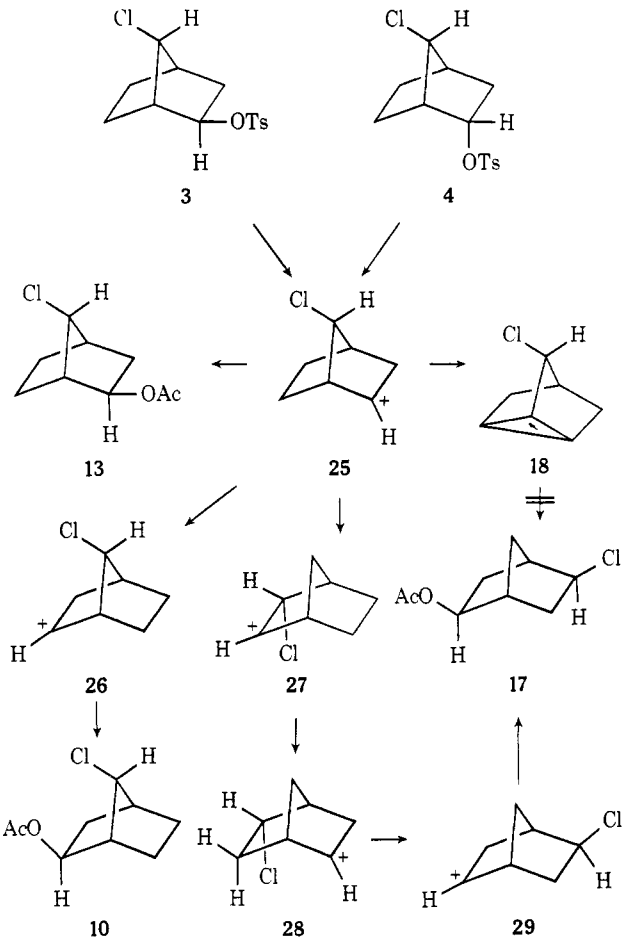
tion by the C_1–C_6 σ bond is not important in the solvolysis of certain norbornyl tosylates. These findings complement those of Brown and coworkers[3,21] who have shown that carbonium ion *stabilizing* groups have relatively little effect on the exo/endo rate ratio.

As we have previously shown[4] the validity of any conclusions based on kinetic data is extremely dependent on the corroborative agreement of the product analysis. In the epimeric pair **1** and **2** the chlorine was syn to the leaving tosylate moiety and might be expected to provide assistance to the loss of endo tosylate through stabilization of the incipient carbonium ion. Although the rate comparison failed to indicate the presence of any rate acceleration due to such neighboring group participation, product studies showed that the solvolysis of **1** and **2** was more complex than might be anticipated on the basis of the kinetic study. Since **1** and **2** gave different product ratios, the two solvolyses must not have passed through a common intermediate. This observation can be contrasted to that for **3** and **4** where virtually identical product mixtures were obtained (indicating the formation of the same intermediate from both **3** and **4**). Since **1** and **2** do not yield the same product mixture, it would seem that some interaction of the syn chloro group must be occurring. If this neighboring group participation is occurring in the transition state for ionization of the tosylate function, the high exo/endo rate ratio would indicate an influence of the syn chloro moiety on the solvolysis of both the exo and endo tosylates. These compensating factors may involve a small amount of anchimeric assistance by the chloro group of **2**, balanced against a small amount of steric acceleration due to the chloro group of **1**.

While the nonidentity of the product mixtures from **1** and **2** detracts from the use of these molecules as models for *exo*- and *endo*-norbornyl tosylates, the identity of the product mixtures from **3** and **4** indicates that these tosylates should be good models. The products formed from **3** and **4** can be readily rationalized in terms of the initial formation of the classical ion **25**. Nucleophilic attack of acetic acid on **25** would give **13**. A 6,2-hydride shift would convert **25** into **26**, which on reaction with acetic acid would produce **10**. Loss of a proton from **25** would give **18**.[22] A Wagner–Meerwein rearrangement would convert 25 into 27 and a hydride shift would convert **27** into **28** which on Wagner–Meerwein rearrangement would give **29**. Collapse of **29** with solvent would then produce **17**. Although it appears that **17** might readily result from the addition of acetic acid to **18**, we were able to demonstrate that **18** was not converted into **17** under the reaction conditions.

Summary

The high exo/endo rate ratio, the formation of the same products, and the absence of any endo products in the solvolysis of **3** and **4** indicate that norbornanes in which the generation of a partial positive charge at C-1 is electronically unfavorable can behave in a fashion very similar to the parent norbornyl tosylates. Although this does not permit one to conclude that the 2-norbornyl cation is classical, it does indicate that high exo/endo rate ratios and exclusive formation of exo products are not unequivocal criteria for postulating the intermediacy of a nonclassical cation in the solvolysis of 2-norbornyl tosylate.



Experimental Section[23]

***syn*-7-Chloro-*exo*-2-hydroxybicyclo[2.2.1]heptane (5).** This alcohol was prepared by the procedure of Roberts, Johnson, and Carboni.[7]

***syn*-7-Chlorobicyclo[2.2.1]heptan-2-one (7).** The ketone **7** was initially prepared by the procedure of Roberts, Johnson, and Carboni.[7] However, an improved procedure involved the preparation of **7** in better yield by Jones oxidation of **5**. To a solution of 6.3 g (0.043 mol) of **5** in 250 ml of reagent grade acetone, 6 *M* chromic acid was added dropwise until the red color persisted (16 ml) This solution was stirred for 1 hr and then the solvent was removed under reduced pressure with no external heating. The residue was dissolved in 500 ml of ether, washed with saturated sodium bicarbonate solution and with water, and dried over anhydrous magnesium sulfate. The solvent was removed by distillation and the residue sublimed at 75° (4 mm) to yield 5.09 g (82%) of **7**.

***anti*-7-Chloro-*exo*-2-hydroxybicyclo[2.2.1]heptane (6).** The alcohol was prepared according to the procedure of Roberts, Johnson, and Carboni.[7]

(19) C. S. Foote, *J. Amer. Chem. Soc.*, **86**, 1853 (1964); P. v. R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

(20) S. H. Liggero, J. J. Harper, P. Schleyer, A. P. Krapcho, and D. E. Horn, *ibid.*, **92**, 3789 (1970); J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. Schleyer, *ibid.*, **92**, 2538 (1970).

(21) It should be noted that the effects of carbonium ion stabilizing groups were determined on *tertiary* norbornyl derivatives where the stability of the carbonium ion would be maximized.

(22) The formation of **18** could also proceed *via* the intermediacy of **26**, **27**, **28**, and **29**.

(23) Boiling points and melting points are uncorrected. Nuclear magnetic resonance spectra were obtained on a Varian Model A-60, A-60A, or HA-100 spectrometer. Gas–liquid partition chromatographic work was performed with an Aerograph HyFi Model A-600 and an Aerograph "Autoprep" Model A-700. Elemental analyses were obtained from the Scandinavian Microanalytical Laboratory, Herlev, Denmark.

anti-**7-Chlorobicyclo[2.2.1]heptan-2-one (11).** The ketone **11** was prepared from **6** by Jones oxidation as described above for **7**, and sublimed at 75° (4 mm) to yield 76% of **11**, mp 86–90° (lit.[7] mp 89–90°).

syn-**7-Chloro-*endo*-2-hydroxybicyclo[2.2.1]heptane (8).** A solution of 8.5 g (0.059 mol) of **7** and 4.9 g of aluminum isopropoxide in 500 ml of isopropyl alcohol was slowly distilled until the distillate no longer gave a positive 2,4-dinitrophenylhydrazine test for acetone. The remaining solvent was removed by distillation. The residue was poured into 1 l. of 5% sodium hydroxide solution and extracted with four 200-ml portions of ether. The combined extracts were dried over anhydrous magnesium sulfate and filtered. The solvent was removed by distillation and the residue sublimed at 75° (2 mm) to yield 6.18 g (72%) of **8**, 95% pure by glpc analysis (10 ft × 3/8 in., 2% XF-1150 on Chromosorb G column at 120°), the major contaminant being **5**. Chromatography on silica gel gave material that was homogeneous upon glpc analysis. Recrystallization from Skelly F gave material melting at 90–93°.

Anal. Calcd for $C_7H_{11}OCl$: C, 57.34; H, 7.51; Cl, 24.23. Found: C, 57.50; H, 7.57; Cl, 24.08.

syn-**7-Chloro-*endo*-2-acetoxybicyclo[2.2.1]heptane (9).** To an ice cold solution of 0.5 g (0.0034 mol) of **8** in 10 ml of pyridine was added 0.6 g (0.0076 mol) of acetyl chloride. After standing overnight at 5° the solution was poured into 250 ml of water and extracted with three 50-ml portions of ether. The combined extracts were washed with dilute hydrochloric acid, with water, and with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Distillation yielded 0.64 g (99%) of **9**, bp 85–87° (2.4 mm). The acetate was purified by preparative glpc (15 ft × 3/8 in., 15% butanediol succinate on Chromosorb G column at 150°), $n^{25}D$ 1.4816.

Anal. Calcd for $C_9H_{13}O_2Cl$: C, 57.29; H, 6.89; Cl, 18.83. Found: C, 57.41; H, 7.00; Cl, 18.71.

syn-**7-Chloro-*exo*-2-acetoxybicyclo[2.2.1]heptane (10).** The acetate **10** was prepared from **5** and purified in the manner described above for **9** in 94% yield, bp 80–82° (1.7 mm), $n^{25}D$ 1.4826.

Anal. Calcd for $C_9H_{13}O_2Cl$: C, 57.29; H, 6.89; Cl, 18.83. Found: C, 57.43; H, 6.97; Cl, 18.70.

anti-**7-Chloro-*endo*-2-hydroxybicyclo[2.2.1]heptane (12).** To a stirred slurry of 1.5 g (0.039 mol) of lithium aluminum hydride in 100 ml of anhydrous ether, a solution of 5.0 g (0.035 mol) of **11** in 25 ml of anhydrous ether was added dropwise over 1 hr. The slurry was stirred for 1 hr and then 6.0 ml of water was added dropwise. After stirring for 3 hr, the solids were removed by filtration and the ether solution dried over anhydrous magnesium sulfate. The drying agent was removed by filtration, the solvent was removed by distillation, and the residue sublimed at 75° (2 mm) to yield 4.41 g (87%) of a mixture of **12** and **6**. Analysis of the product mixture on a 10 ft × 3/8 in. 2% XF-1150 on Chromosorb G column at 120° showed the ratio of **12**:**6** was 9:1. The *endo*-alcohol **12** was purified by preparative glpc on a 10 ft × 3/8 in. 25% XF-1150 on Chromosorb P column at 150° Recrystallization from Skelly F gave a sample melting at 84–86°.

Anal. Calcd for $C_7H_{11}OCl$: C, 57.34; H, 7.51; Cl, 24.23. Found: C, 57.30; H, 7.56; Cl, 23.91.

anti-**7-Chloro-*exo*-2-acetoxybicyclo[2.2.1]heptane (13).** The acetate **13** was prepared from **6** and purified in the manner described above for **9** in 89% yield, bp 78–79° (1.7 mm), $n^{25}D$ 1.4808.

Anal. Calcd for $C_9H_{13}O_2Cl$: C, 57.29; H, 6.89; Cl, 18.83. Found: C, 57.43; H, 6.97; Cl, 18.53.

anti-**7-Chloro-*endo*-2-acetoxybicyclo[2.2.1]heptane (14).** The acetate **14** was prepared from **12** and purified in the manner described above for **9** in 86% yield, bp 83–85° (2.4 mm), $n^{25}D$ 1.4821.

Anal. Calcd for $C_9H_{13}O_2Cl$: C, 57.29; H, 6.89; Cl, 18.83. Found: C, 57.32; H, 7.01; Cl, 18.63.

syn-**7-Chloro-*exo*-2-tosyloxybicyclo[2.2.1]heptane (1).** The tosylate **1** was prepared from **5** according to the procedure of Roberts, Johnson, and Carboni,[7] mp 61–62.5° (lit. mp 51–52°[7] and 61.0–61.5°[8]).

anti-**7-Chloro-*exo*-2-tosyloxybicyclo[2.2.1]heptane (3).** The tosylate **3** was prepared from **6** according to the procedure of Roberts, Johnson, and Carboni,[7] mp 66–66.5° (lit. mp 64–65.4°[7] and 65–65.5°[8]).

anti-**7-Chloro-*endo*-2-tosyloxybicyclo[2.2.1]heptane (4).** To an ice cold solution of 3.0 g (0.02 mol) of **12** in 40 ml of pyridine was added 7.0 g (0.038 mol) of tosyl chloride. The solution was allowed to stand overnight at 5° and then poured into 500 ml of water. The aqueous solution was extracted with three 150-ml portions of chloroform. The combined extracts were washed with dilute hydrochloric acid solution, with water, and with saturated sodium chloride solution, and dried over anhydrous magnesium sulfate and the drying agent was removed by filtration. The solvent was removed under reduced pressure and the resulting solid was recrystallized from Skelly F–ether to give 3.5 g (55%) of **4**, mp 83.5–84.5°.

Anal. Calcd for $C_{14}H_{17}O_3ClS$: C, 55.91; H, 5.66; Cl, 11.81; S, 10.65. Found: C, 56.00; H, 5.77; Cl, 11.99; S, 10.51.

syn-**7-Chloro-*endo*-2-tosyloxybicyclo[2.2.1]heptane (2).** The tosylate **2** was prepared from **8** according to the procedure described above for **4** in 73% yield. This tosylate melted below room temperature and was purified by chromatography on silica gel, fo 'owed by molecular distillation.

Anal. Calcd for $C_{14}H_{17}O_3ClS$: C, 55.91; H, 5.66; Cl, 11.81; S, 10.65. Found: C, 55.69; H, 5.48; Cl, 11.51; S, 10.79.

Kinetics. Reagents. Anhydrous acetic acid was prepared by refluxing a solution of acetic anhydride and sodium acetate in glacial acetic acid for 24 hr and subsequent fractional distillation in a dry atmosphere. Standard sodium acetate in acetic acid (*ca.* 0.1 *M*) was prepared by the careful addition of anhydrous acetic acid to a solution of anhydrous sodium carbonate in acetic anhydride, such that *ca.* 1% acetic anhydride remained after the water of neutralization was removed, followed by refluxing in a dry atmosphere for 5 hr[24] (calculated to be 1.325 g of anhydrous sodium carbonate and 3.78 g of acetic anhydride diluted to 250 ml with anhydrous acetic acid). Standard perchloric acid in acetic acid (*ca.* 0.02 *M*) used in titrating acetolysis aliquots was prepared by the careful addition of 70% perchloric acid to a solution of anhydrous acetic acid and acetic anhydride, such that 1% acetic anhydride remained after the water was removed, followed by standing at room temperature for 12 hr. The molarity of the standard perchloric acid in acetic acid was determined by titrating an aliquot *vs.* potassium acid phthalate (primary standard) in anhydrous acetic acid using Bromophenol Blue as the indicator.

Procedure. The kinetic procedure followed was essentially that of Winstein and coworkers.[25] All rates were determined using a calculated infinity titer.

Acetolysis Product Analysis of *anti*-7-Chloro-*exo*-2-tosyloxybicyclo[2.2.1]heptane (3). A solution of 0.0442 g of **3** in 2 ml of 0.1 *N* sodium acetate in acetic acid was sealed in a solvolysis tube and heated at 100° for 10 min ($t_{1/2}$ = 24 min). After cooling to room temperature the solution was poured into 40 ml of water and neutralized by the addition of 5 g of sodium bicarbonate. The aqueous solution was extracted with three 15-ml portions of ether; the combined extracts were dried over anhydrous magnesium sulfate. Integration[26] of a glpc trace of this solution showed the following percentages of products: 4% of **18**, 70% of **13**, 9% of **17**, 14% of **10**, and 3% of several unidentified components. Product identity was established by isolation by preparative glpc (5 ft × 3/8 in. 30% DEGS on Chromosorb P column at 140°), and comparison with authentic samples in the case of **13** and **10**, and by comparison of glpc retention times on three different columns (10 ft × 1/8 in. 15% DEGS on Chromosorb P column at 160°; 10 ft × 1/8 in. 15% UCON on firebrick column at 190°; and 10 ft × 1/8 in. 3% FFAP on Chromosorb G column at 125°) for **18** and **17**. No endo acetates **9** and **14** could be detected (<0.1%).

Acetolysis Product Analysis of *syn*-7-Chloro-*exo*-2-tosyloxybicyclo[2.2.1]heptane (1). A solution of 0.0453 g of **1** in 2 ml of 0.1 *N* sodium acetate in acetic acid was sealed in a solvolysis tube and heated at 100° for 10 min ($t_{1/2}$ = 19 min at 100°). The solution was worked up and analyzed as described above for **3** and found to yield the following products: 2% of **18**, 42% of **13**, 9% of **17**, 45% of **10**, and 2% of several unidentified compounds. Product identity was established as above for **3**. No endo acetates **9** and **14** could be detected (<0.1%).

Acetolysis Product Analysis of *anti*-7-Chloro-*endo*-2-tosyloxybicyclo[2.2.1]heptane (4). A solution of 0.0422 g of **4** in 2 ml of 0.1 *N* sodium acetate in acetic acid was sealed in a solvolysis tube and heated at 130° for 10 min ($t_{1/2}$ = 43 min at 130°). The solution was worked up and analyzed as described above for **3** and found to yield the following products: 7% of **18**, 69% of **13**, 8% of **17**, 11% of **10**, and 2% of several unidentified compounds. Product identity was established as above for **3**. No endo acetates **9** and **14** could be detected (<0.1%).

(24) P. D. Bartlett and W. P. Giddings, *J. Amer. Chem. Soc.*, **82**, 1240 (1960).

(25) S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

(26) The percentages of products were corrected for differences in glpc detector response.

Acetolysis Product Analysis of *syn*-7-Chloro-*endo*-2-tosyloxybicyclo[2.2.1]heptane (2). A solution of 0.0412 g of **2** in 2 ml of 0.1 *N* sodium acetate in acetic acid was sealed in a solvolysis tube and heated at 130° for 20 min ($t_{1/2}$ = 93 min at 130°). The solution was worked up and analyzed as described above for **3** and found to yield the following products: 16% of **18**, 42% of **13**, 8% of **17**, 24% of **10**, and 9% of several unidentified compounds. Product identity was established as described above for **3**. No endo acetates **9** and **14** could be detected (<0.1%).

Stability of 3-Chlorotricyclo[2.2.1.$0^{2,6}$]heptane (18) to Acetolysis Conditions. A solution of 0.0165 g (0.00013 mol) of **18** and 0.0123 g (0.000065 mol) of *p*-toluenesulfonic acid monohydrate in 1 ml of 0.1 *N* sodium acetate in acetic acid was sealed in a solvolysis tube and heated at 100° for 4 hr. The solution was cooled to room temperature, poured into 20 ml of water, and neutralized with 2.5 g of sodium bicarbonate. The aqueous solution was extracted with three 10-ml portions of ether and the combined extracts were dried over anhydrous magnesium sulfate. Analysis of this solution by glpc (10 ft × 1/8 in. 15% DEGS on Chromosorb P column at 160°) showed that about 50% of **18** had decomposed to give several unidentified products in about 25% yield and 25% of **10**. However, no **17** could be detected in the solution.

Stability of 7-Chloro-2-acetoxybicyclo[2.2.1]heptanes to Acetolysis Conditions. A solution of 0.0594 g of **10**, 0.0584 g of **13**, 0.0613 g of **14** and 0.0455 g of **9** in 10 ml of 0.1 *N* sodium acetate in acetic acid was prepared. One-milliliter aliquots of this solution were sealed in solvolysis tubes and heated to 120°. The tubes were worked up in the usual manner. Analysis of the solutions by glpc (10 ft × 1/8 in. 15% DEGS on Chromosorb P column at 160°) showed no decomposition of any of the acetates after 20 min at 120°, and no decomposition after 70 min. However, after several hours at this temperature, decomposition began to occur.

3-Chlorotricyclo[2.2.1.$0^{2,6}$]heptane (18). The chloride **18** was obtained as a by-product in the preparation of **5**, as described by Roberts, Johnson, and Carboni,[7] and purified by preparative glpc (5 ft × 3/8 in. 30% DEGS on Chromosorb P column at 100°).

5-Hydroxybicyclo[2.2.1]hept-2-ene (19). A solution of 20 g (0.13 mol) of 5-acetoxybicyclo[2.2.1]hept-2-ene in 50 ml of anhydrous ether was added dropwise to a slurry of 5.0 g (0.13 mol) of lithium aluminum hydride in 200 ml of anhydrous ether over a period of 1 hr. The solution was stirred for an additional hour and then 20 ml of water was added dropwise. After stirring overnight the solution was filtered and dried over anhydrous magnesium sulfate. Removal of solvent by distillation yielded 14.5 g of crude **19**.

***exo*-2-Chloro-*exo*-5-hydroxybicyclo[2.2.1]heptane (20).** Dry hydrogen chloride gas was bubbled through a solution of 14.5 g (0.14 mol) of **19** in 200 ml of anhydrous ether. The reaction was monitored by glpc (10 ft × 1/8 in. 3% FFAP on Chromosorb G column at 170°). After 5 hr the reaction had gone to about 90% completion with the formation of two products, **20** and **21**, in a 1:2 ratio. The ether solution was washed twice with water, with saturated sodium bicarbonate solution, and with saturated sodium chloride solution and dried over anhydrous magnesium sulfate. Removal of the drying agent followed by short-path distillation yielded 5.8 g (31%) of **20** and **21**, bp 73–92° (1.4 mm).

A solution of 2.0 g (0.014 mol) of this mixture, 4.0 g (0.019 mol) of aluminum isopropoxide, and 0.5 ml of acetone in 50 ml of toluene was refluxed for 24 hr. This solution was poured into 250 ml of 10% aqueous hydrochloric acid solution and the organic phase separated. The aqueous phase was washed with two 75-ml portions of ether. The combined organic phases were washed with water and with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered. Analysis of the filtrate by glpc, on the above described column, showed **20** and **21** in a 2:1 ratio. Distillation yielded 1.6 g (80%) of the mixture, bp 89–92° (2 mm). The exo alcohol **20** was purified by preparative glpc (10 ft × 3/8 in. 3% FFAP on Chromosorb G column at 170°).

Anal. Calcd for $C_7H_{11}ClO$: C, 57.30; H, 7.56; Cl, 23.91. Found: C, 57.23; H, 7.55; Cl, 24.24.

***exo*-2-Chloro-*exo*-5-acetoxybicyclo[2.2.1]heptane (17).** To an ice cold solution of 1.0 g (0.0068 mol) of **20** and **21** (2:1) in 20 ml of pyridine, 2.0 g (0.02 mol) of acetic anhydride was added and the solution allowed to stand overnight at 5°. The solution was poured into 500 ml of water and extracted with three 150-ml portions of ether. The combined extracts were washed with dilute hydrochloric acid solution, with water, and with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and filtered. Distillation yielded 1.0 g (78%) of **17**, bp 72–89° (1.5 mm), contaminated with the epimeric endo acetate. The acetate **17** was obtained pure by two passages through a preparative glpc (5 ft × 3/8 in. 30% DEGS on Chromosorb P column at 145°), n^{25}D 1.4818.

Anal. Calcd for $C_9H_{13}ClO_2$: C, 57.29; H, 6.89; Cl, 18.83. Found: C, 57.37; H, 6.94; Cl, 18.80.

***exo*-5-Chlorobicyclo[2.2.1]heptan-2-one (22).** To a solution of 5.0 g (0.034 mol) of **20** and **21** (1:2) in 200 ml of reagent grade acetone, 6 *N* chromic acid was added dropwise until the red color persisted. The solution was stirred for an additional hour and then concentrated under reduced pressure. The residue was dissolved in ether and filtered to remove solids. The ether solution was washed with water and with saturated sodium bicarbonate solution, dried over anhydrous magnesium sulfate, and filtered. Removal of the solvent and distillation yielded 3.6 g (74%) of **22**, bp 75–98° (10 mm). Analysis by glpc (10 ft × 1/8 in. 19% Carbowax 20M on Chromosorb W column at 150°) showed only one major peak.

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