**Solvolysis of *trans*-Bicyclo[6.1.0]nonyl *cis*-2-Tosylate in 80% Aqueous Acetone.** An ice-cold solution of 0.13 g (1 mmol) of *N,N*-diisopropylethylamine and 17 ml of 80% aqueous acetone was poured into a tube containing 0.15 g (0.51 mmol) of *trans*-bicyclo-[6.1.0]nonyl *cis*-2-tosylate. The tube was sealed and immersed in an oil bath at 80°. After 2 hr the tube was removed from the bath, cooled, and opened. After the same treatment as described above, the products were separated by vpc on the Carbowax column. The products were *trans*-bicyclo[6.1.0]nonan-*cis*-2-ol (39%) and cyclononen-4-ol (60%).

**Solvolysis of *cis*-Bicyclo[5.2.0]nonyl *trans*-8-Tosylate in 80% Aqueous Acetone.** The solvolysis was carried out as described above. The products were *trans*-bicyclo[6.1.0]nonan-*trans*-2-ol (76%), *cis*-bicyclo[5.1.0]octane-*trans*-8-methanol (12%), and *cis*-bicyclo[5.2.0]nonan-*trans*-8-ol (8%).

**Solvolysis of *cis*-Bicyclo[5.1.0]octane *trans*-8-Methyl Tosylate in 80% Aqueous Acetone.** The solvolysis was carried out as described above. The products were *trans*-bicyclo[6.1.0]nonan-*trans*-2-ol (57%), *cis*-bicyclo[5.1.0]octane-*trans*-8-methanol (24%), and *cis*-bicyclo[5.2.0]nonan-*trans*-8-ol (9%).

**Solvolyses of 2-Deuteriobicyclo[6.1.0]nonyl-2 Derivatives.** The solvolyses were carried out under the same conditions as before. The reactions were stopped after 2.5 half-lives and treated as described above after the removal of unreacted or rearranged 3,5-dinitrobenzoates. Products were analyzed on a 20 ft × 3/8 in. 20% Carbowax 20M on 60–70 Anachrom column at 170°. The *trans,trans*-3,5-dinitrobenzoate (Ia-*d*) solvolyzed at 80° gave three products. The main product (80%), the trans,trans alcohol, showed 65 ± 3% scrambling of deuterium by nmr. The *trans,cis*-tosylate, solvolyzed at 80° for the same length of time as the *trans,trans*-3,5-dinitrobenzoate (Ia-*d*), afforded two products (the trans,cis alcohol, 36%, and cyclononen-4-ol, 62%), whose nmr spectra showed no appreciable deuterium scrambling (0 ± 4%, 0 ± 3%). The *cis,trans*-3,5-dinitrobenzoate (IIIa-*d*) solvolyzed at 120° gave two products. The main product (96%), the cis,trans alcohol, showed no appreciable deuterium scrambling (0 ± 3%). The *cis,cis*-3,5-dinitrobenzoate (IVa-*d*) solvolyzed at 100° afforded two products (the cis,cis alcohol, 75%, and cyclononen-4-ol, 25%), whose nmr spectra showed no appreciable deuterium scrambling (0 ± 3%, 0 ± 2%).

**Kinetic Method.** Acetone was purified by distillation from potassium permanganate and degassed by boiling for several minutes. Distilled water was degassed in the same manner. The solvents and solutions were kept under a nitrogen atmosphere to minimize oxidation of the solvent at higher temperature. In all cases, the solvent was 80% acetone by volume.

In each case, 60 ml of a 0.006 *M* solution of the 3,5-dinitrobenzoate was prepared and 3.3-ml portions were sealed in ampoules. A set of ampoules was immersed in an oil bath at the appropriate temperature. Allowing 10 min for temperature equilibration, the zero point was taken. The ampoules were removed from the bath and plunged into ice–water to stop the solvolysis. After warming to room temperature, a 3.00-ml portion of the solution was removed and titrated with 0.0050 *M* sodium hydroxide solution to a bromothymol blue end point. Infinity titers were determined after 10 half-lives.

# Reactions of Trans-Fused Cyclopropanes. The Synthesis and Solvolysis of the Epimeric 2-Hydrovy-*trans*-bicyclo[6.1.0]nonane *p*-Nitrobenzoates[1]

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*Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.* *Received December 10, 1970*

**Abstract:** The epimeric 2-hydroxy-*trans*-bicyclo[6.1.0]nonanes have been synthesized and their respective *p*-nitrobenzoates have been solvolyzed in 30:70 water–dioxane. At 100° the trans,trans isomer solvolyzed $1.2 \times 10^4$ times faster than the cis,trans isomer. In addition, the epimeric *p*-nitrobenzoates produced different product mixtures on solvolysis, indicating that the solvolyses of the epimeric *p*-nitrobenzoates followed different mechanistic paths. The rate differences and the divergence of products are discussed in terms of the conformations of the epimeric *p*-nitrobenzoates. These, in turn, are related to the steric requirements for cyclopropyl participation in the formation of cyclopropylcarbinyl cations. Our results would appear to provide strong evidence for the necessity of backside participation by the cyclopropyl group in the formation of cyclopropylcarbinyl cations.

Various groups have investigated the generation of carbonium ion centers adjacent to cyclopropyl rings when the cyclopropyl moiety was part of a cis-fused bicyclo[*n*.1.0]alkane derivative.[5] The objective of these studies was to determine the mode of interaction of the cyclopropyl ring with the incipient carbonium ion. When *n* was small, such as in the bicyclo[3.1.0]-hexyl system, prevailing evidence indicated that a single carbonium ion intermediate was formed.[5a-c] When *n* was somewhat larger, as in the *cis*-bicyclo[5.1.0]octyl and *cis*-bicyclo[6.1.0]nonyl systems, it would appear that two distinct cationic intermediates were formed when the epimeric 2-substituted derivatives of these systems were solvolyzed.[5d,e,6] In view of the conformational mobility of the eight-membered ring of the *cis*-bicyclo[6.1.0]nonane skeleton, the exact stereochemical relationship between the leaving group at C-2 and the neighboring cyclopropyl ring was undefined. In this regard we felt it would be of interest to study the corresponding solvolytic processes in the much more rigid *trans*-bicyclo[6.1.0]nonanes, where the trans ring

(1) Paper XXV on "The Chemistry of Bent Bonds." For the previous paper in this series, see P. G. Gassman and J. S. Atkins, *J. Amer. Chem. Soc.*, **93**, 4597 (1971).

(2) Alfred P. Sloan Foundation Research Fellow, 1967–1969.

(3) Petroleum Research Fund Research Fellow, 1969–1970; Wm. Lloyd Evans Fellow, 1970–1971.

(4) Goodyear Foundation Fellow, 1968–1969; Dow Chemical Fellow, 1969–1970.

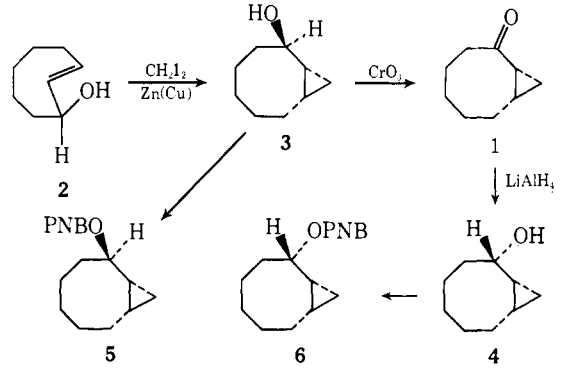
(5) (a) G. H. Schmid and A. Brown, *Tetrahedron Lett.*, 4695 (1968); (b) P. R. Brook, R. M. Ellam, and A. S. Bloss, *Chem. Commun.*, 425 (1968); (c) H. L. Goering and K. E. Rubenstein, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 28–31, 1966, p KO11; (d) L. E. Friedrich and F. R. Wight, *J. Amer. Chem. Soc.*, **92**, 1807 (1970); (e) C. Dale Poulter, E. C. Friedrich, and S. Winstein, *ibid.*, **92**, 4274 (1970).

(6) See also A. C. Cope, S. Moon, and C. H. Park, *ibid.*, **84**, 4850 (1962).

fusion greatly decreases the ability of the leaving group to assume different conformational relationships to the cyclopropyl ring. We now wish to report the details of the synthesis and solvolysis of the epimeric 2-hydroxy-*trans*-bicyclo[6.1.0]nonane *p*-nitrobenzoates.[7,8]

**Synthesis of *p*-Nitrobenzoates.** *trans*-Bicyclo[6.1.0]-nonan-2-one (**1**) was prepared by a modification of the procedure of DePuy and Marshall[9] as shown in Chart I.

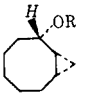
**Chart I**




Starting with *trans*-cycloocten-3-ol (**2**),[10] we prepared **3** in 62% yield[11] using methylene iodide and zinc–copper couple.[12] Oxidation of **3** with Jones reagent[13] gave **1** in 67% yield. Reduction of **1** with lithium aluminum hydride in ether gave an 85% yield of a 95:5 mixture of **4** to **3**.

The relative stereochemical relationships of the hydroxyl functions to the cyclopropyl rings of **3** and **4** were established on the basis of both chemical and spectroscopic evidence. Examination of models of **1** indicated that hydride reduction should occur from the least hindered side of the carbonyl to yield the more hindered alcohol. In the case of **1**, this means that the resulting hydroxyl function should be cis to the nearest cyclopropyl bond on the eight-membered ring.[14] This required that the addition of methylene to **2** must have occurred in a manner which placed the hydroxyl function trans to the nearest cyclopropyl bond on the cyclooctyl ring. Ample precedent exists for this type of addition in the observations of Winstein and coworkers[15] who found that the Simmons–Smith reaction[16] on 3-hydroxycycloheptene was not stereospecific and that the additions to 3-hydroxycyclooctene and 3-hydroxycyclononene occurred with the hydroxyl group directing the methylene addition to the side of the ring trans to the hydroxyl. This is a complete reversal from the experimental observations made on the directive effect of the hydroxyl group in the 3 position of cyclopentenes and cyclohexenes.[15] Spectroscopic evidence for the stereochemical assignments was obtained from the nmr spectra of **3** and **4**. The proton at C-2 of **3** appeared as a multiplet at $\tau$ 6.95 while the C-2 proton of **4** was found at $\tau$ 5.88. As shown in Table I this shift of approximately 1 ppm in the position of the C-2 proton occurred in both the *cis*- and *trans*-bicyclo[6.1.0]nonan-2-ols and in their respective *p*-nitrobenzoates. Wiberg and Nist have previously studied the shielding effect of the cyclopropyl group on neighboring hydrogens.[17] They found that a neighboring cyclopropyl ring shields protons which are above and below the plane of the three-membered ring and deshields those which are in the plane of the ring. Owing to the large degree of conformational freedom in the *cis*-bicyclo[6.1.0]nonanes, little is known with certainty about the preferred conformation of the eight-membered ring in relation to the cyclopropyl moiety. However, the nmr observations listed below would indicate significant similarities between the C-2 protons of the *cis*- and *trans*-bicyclo-[6.1.0]nonan-2-ols. The same holds true for the derived *p*-nitrobenzoates.

**Table I.** Nmr Chemical Shift of the C-2 Proton in 2-Hydroxybicyclo[6.1.0]nonanes and in the Corresponding *p*-Nitrobenzoates

| Compd | Ppm relative to tetramethylsilane in $CCl_4$ | |
|---|---|---|
| | R = H | R = $O_2N$–C$_6$H$_4$–C(=O)– |
|  | 3.18 (3.02[a,b]) | 4.8 (4.9[a]) |
|  | 4.40 (4.30[a,b]) | 5.8 (5.82[a]) |
|  | 3.05 | 4.5 |
|  | 4.12 | 5.6 |

[a] See ref 5e. [b] See ref 15.

Whereas the *cis*-bicyclo[6.1.0]nonan-2-ols have a great deal of conformational freedom, the corresponding *trans*-bicyclo[6.1.0]nonan-2-ols are rigidly held due to the nature of the trans ring fusion. Examination of models indicated that the two conformations shown by **7** and **8** would represent reasonable conformational energy minima. Minimization of torsional and nonbonding interaction predicted that **7** should be of considerably lower energy than **8**. In view of the extremely rigid nature of these structures it would be

**7** **8**

(7) For a preliminary report of part of this work, see P. G. Gassman and E. A. Williams, Abstracts, Second Central Regional Meeting of the American Chemical Society, Columbus, Ohio, June 3–5, 1970, p 50.

(8) Similar results have been obtained by K. B. Wiberg and T. Nakahira, *Tetrahedron Lett.*, 3759 (1970). We wish to thank Professor Wiberg for informing us of his results prior to publication and for agreeing to simultaneous publication. See K. B. Wiberg and T. Nakahira, *J. Amer. Chem. Soc.*, **93**, 5193 (1971).

(9) C. H. DePuy and J. L. Marshall, *J. Org. Chem.*, **33**, 3326 (1968).

(10) G. H. Whitham and M. Wright, *Chem. Commun.*, 294 (1967).

(11) This material consisted of 97% **3** contaminated with 3% **4**.

(12) E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

(13) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

(14) This observation is similar to that made for the lithium aluminum hydride reduction of *cis*-bicyclo[6.1.0]nonan-2-one.[5e]

(15) C. Dale Poulter, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 6892 (1969).

(16) H. E. Simmons and R. D. Smith, *ibid.*, **80**, 5323 (1958).

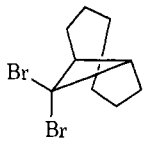
(17) K. W. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961).

Table II. Solvolysis Rates of the *p*-Nitrobenzoates of the Four Epimeric 2-Hydroxybicyclo[6.1.0]nonanes in 30:70 Water–Dioxane

| Compd | Temp, °C | Rate, $sec^{-1}$ | $\Delta H^{\ddagger}$, kcal/mol | $\Delta S^{\ddagger}$, eu | $k_{rel}^{100°}$ |
|---|---|---|---|---|---|
| **6** | 230.00 ± 0.06 | $(1.13 \pm 0.01) \times 10^{-3}$ | | | |
| | 215.00 ± 0.05 | $(5.39 \pm 0.11) \times 10^{-4}$ | 27.9 | −17 | 1 |
| | 200.00 ± 0.05 | $(1.81 \pm 0.03) \times 10^{-4}$ | | | |
| | 100.00[a] | $5.25 \times 10^{-8}$ | | | |
| **5** | 110.00 ± 0.02 | $(1.77 \pm 0.05) \times 10^{-3}$ | | | |
| | 95.00 ± 0.02 | $(3.20 \pm 0.03) \times 10^{-4}$ | 27.1 | −1 | 12,400 |
| | 80.00 ± 0.02 | $(7.88 \pm 0.15) \times 10^{-5}$ | | | |
| | 100.00[a] | $6.52 \times 10^{-4}$ | | | |
| **11** | 185.00 ± 0.02 | $(1.87 \pm 0.06) \times 10^{-3}$ | | | |
| | 170.00 ± 0.02 | $(7.01 \pm 0.06) \times 10^{-4}$ | 22.1 | −24 | 112 |
| | 155.00 ± 0.02 | $(3.20 \pm 0.01) \times 10^{-4}$ | | | |
| | 100.00[a] | $5.88 \times 10^{-6}$ | | | |
| **10** | 145.00 ± 0.03 | $(1.45 \pm 0.01) \times 10^{-3}$ | | | |
| | 130.00 ± 0.02 | $(2.96 \pm 0.01) \times 10^{-4}$ | 26.0 | −10 | 500 |
| | 115.00 ± 0.02 | $(1.20 \pm 0.02) \times 10^{-4}$ | | | |
| | 100.00[a] | $2.62 \times 10^{-5}$ | | | |

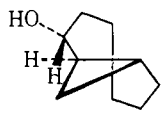
[a] Extrapolated rate from other temperatures.

anticipated that the energy barrier for interconversion of **7** and **8** would be quite high and that the stable arrangement would be that represented by **7**. In support of this theory, recent X-ray studies have shown that 9,9-dibromo-*trans*-bicyclo[6.1.0]nonane has the structure shown by **9**.[18] As shown below, when **3** and **4** are con-

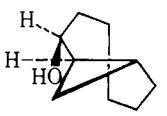



**9**

sidered in terms of the conformation given by **7**, one of the substituents at C-2 is held over the cyclopropyl ring while the other substituent is held away from the ring. Thus in **3**, the proton at C-2 is held above the ring and




**3**




**4**

should be shielded relative to the C-2 proton in **4** which is not held over the cyclopropyl ring and as a result appears 1.07 ppm further downfield. This would appear to confirm the assignments made on the basis of the chemical reactions discussed above.

The epimeric *p*-nitrobenzoates, **5** and **6**, were prepared from **3** and **4**, respectively, by standard procedures. We have also prepared the epimeric *p*-nitrobenzoates of *cis*-2-hydroxy-*cis*-bicyclo[6.1.0]nonane (**10**) and *trans*-2-hydroxy-*cis*-bicyclo[6.1.0]nonane (**11**) by procedures which turned out to be virtually identical with those recently published.[5e]

**Kinetics and Product Studies.** The solvolyses of **5**, **6**, **10**, and **11** were studied in 30:70 water–dioxane with end point detection by titration of liberated *p*-nitrobenzoic acid with aqueous sodium hydroxide to a pH 8 end point (determined potentiometrically). All solvolyses gave good pseudo-first-order kinetics through at least 65% reaction. If acid-catalyzed acyl-oxygen cleavage were complicating the reaction, an increasing rate of reaction should have been observed as the reaction proceeded to generate *p*-nitrobenzoic acid. No such increase in rate was noted. Additional evidence against acyl-oxygen cleavage was obtained through the methanolysis of **5** and **6** which gave less than 1% alcoholic products in the presence of the 2,6-lutidine buffer. The results of our kinetic studies are shown in Table II.

The most striking facets of the kinetic data presented in Table II are the large rate differences between the two trans-fused isomers, **5** and **6**, the small rate difference of five between the two cis-fused isomers, and that **6** is *ca.* $10^2$ times slower than **11** while **5** is *ca.* $10^2$ times faster than **11**. The difference in rate between **5** and **6** of $>10^4$ indicated that the rigid stereochemistry of the *trans*-bicyclo[6.1.0]nonane skeleton exerts a dramatic influence on the rate of solvolysis.[19] Since the rates of ionization of the epimeric *p*-nitrobenzoates of the *cis*-bicyclo[6.1.0]nonan-2-ols differed[20] by only a factor of 5, the large rate difference between **5** and **6** must be due to the conformationally fixed relationship of the ester function to the cyclopropyl ring in **5** and **6**.

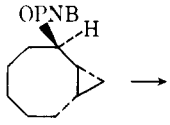
Product studies were carried out in the presence of 2,6-lutidine in order to neutralize the *p*-nitrobenzoic acid since some of the reaction products were shown to rearrange in the absence of a buffer. In view of the recently published product studies of the solvolysis of **10** and **11** in 80% acetone–water, we will not discuss our product studies on the solvolysis of **10** and **11** in 70:30 dioxane–water in detail. It is sufficient to note that our observations agree with the results obtained in acetone–water.[5e,21] The solvolysis of **5** was relatively straight-

(18) S. H. Simonsen, B. J. Bowen, and R. D. Bach, unpublished results. We wish to thank Professor Bach for informing us of these results prior to publication.

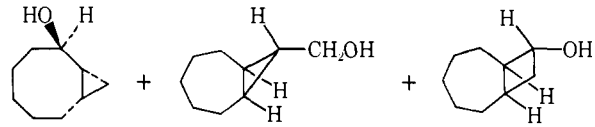
(19) Wiberg and Nakahira have found a rate difference of 18,200 at 100° for the solvolysis of the 3,5-dinitrobenzoates of **3** and **4** in 80% aqueous acetone.[8]

(20) S. Winstein and coworkers have found a rate difference of 23 for the solvolysis of **10** and **11** in 80% acetone–water. The reason that we only note a difference of 5 in rate while other workers noted a difference of 23 may be due to the difference in solvent systems. We were using 70:30 dioxane–water while the comparable studies were made in 80:20 acetone–water.

(21) We observed that **10** gave a 52% yield of *cis*-2-hydroxy-*cis*-bicyclo[6.1.0]nonane and a 31% yield of 4-hydroxy-*cis*-cyclononene at 145°, while **11** gave a 93% yield of *trans*-2-hydroxy-*cis*-bicyclo[6.1.0]-nonane and trace amounts of the epimeric 8-hydroxy-*trans*-bicyclo-[5.2.0]nonanes at 185°. Both studies were in 70:30 dioxane–water buffered with 2,6-lutidine. It is interesting to note that in 70:30 dioxane–water we observed good pseudo-first-order kinetics through 65% reaction using calculated infinity titers. Beyond 65% reaction a slight curvature of the rate plot could be detected indicating a slowing of the rate of generation of acid in the solvolysis of **10**. However, it

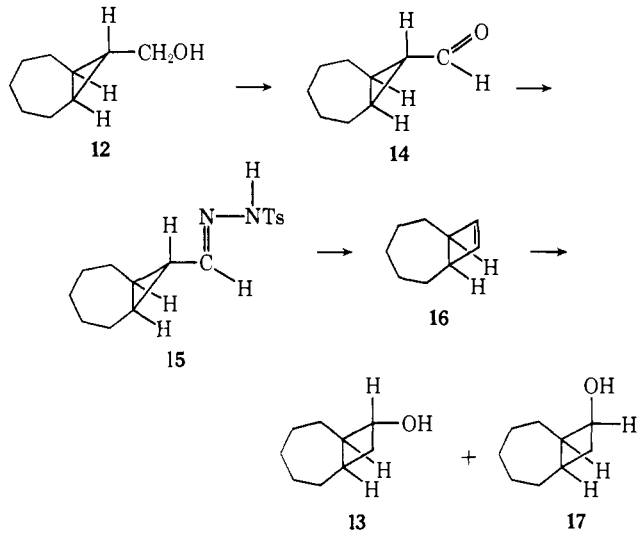


5



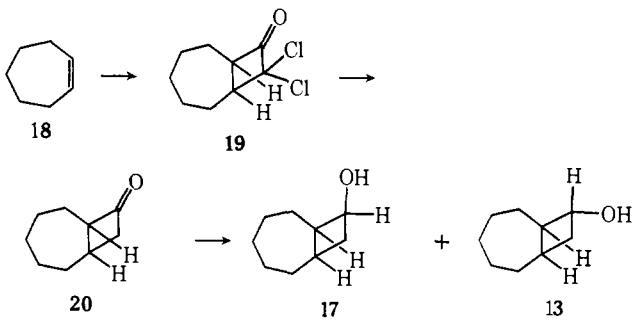
3 12 13

forward in that only **3**, **12**, and **13** were obtained in yields of 77, 10, and 5%, respectively. The identification of **3** was accomplished through isolation and spectral comparison with an authentic sample. The primary carbinol **12** was isolated by preparative vpc and shown to be identical in all respects with an authentic sample of **12** prepared according to the method of Kirmse and Pook.[22] Collins oxidation[23] of **12** gave the aldehyde **14** which was converted to **15**. Treatment of **15** with sodium hydride followed by pyrolysis gave **16**.[22] Hydroboration of **16** gave a mixture of the



12 14 15 16 13 17

epimeric 8-hydroxy-*cis*-bicyclo[5.2.0]nonanes with **13** and **17** being formed in the ratio of 4:1, respectively An alternate synthesis of **13** and **17** involved the addition of dichloroketene to cycloheptene (**18**) to give **19** in



18 19 20 17 13

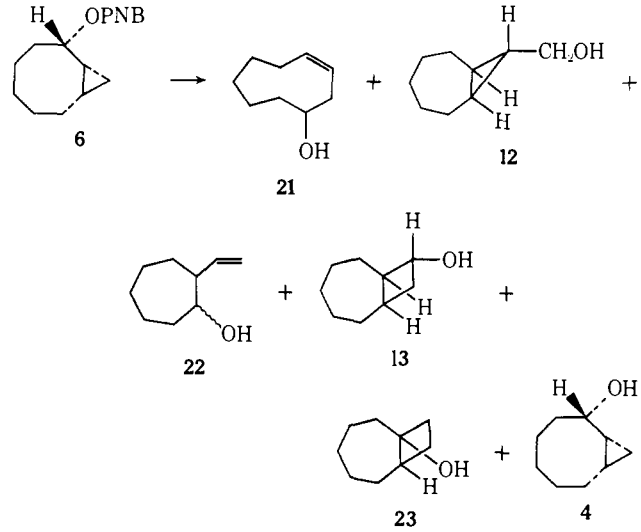
would appear from the kinetic data and from the product studies that internal return as observed by Winstein and coworkers[15] to the extent of 16% for **10** in 80:20 acetone–water at 100° was less significant in 70:30 dioxane–water at 145°.

(22) W. Kirmse and K. H. Pook, *Chem. Ber.*, **98**, 4022 (1965).

(23) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968).

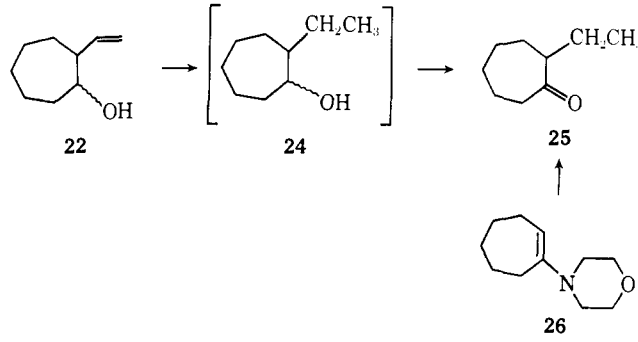
42% yield.[24] Reduction of **19** with tri-*n*-butyltin hydride gave **20** in 60% yield. Lithium aluminum hydride reduction of **20** gave an 85% yield of a 2:1 mixture of **17** to **13** confirming the stereochemical assignments in the case of the hydroboration of **16**. The sample of **13** isolated from the solvolysis mixture was identical in all respects with the material prepared synthetically.

The solvolysis of **6** was quite complex. Product studies in 2,6-lutidine buffered aqueous dioxane gave 18% **21**, 17% **12**, 12% **22**, 10% **13**, 10% **23**, and 9% **4** for an overall yield of 76%. Compounds **4**, **12**, and **13** were identified by isolation and comparison with authentic samples. Authentic samples of **21** and **23**



6 21 12 22 13 23 4

were prepared according to literature procedures[5e,25] and shown to be identical with the samples isolated from the solvolysis mixture by preparative vpc. The stucture of **22** was established by a combination of spectral and chemical evidence. The nmr spectrum of **22** showed a one-hydrogen multiplet at $\tau$ 4.51 for the nonmethylene proton of the vinyl group. The terminal methylene group hydrogens appeared at $\tau$ 4.80 and 4.98 as a quartet and triplet, respectively, while the proton on the same carbon as the hydroxyl appeared at $\tau$ 6.55. Reduction of **22** over 5% Pd/C gave **24**, which was



22 24 25 26

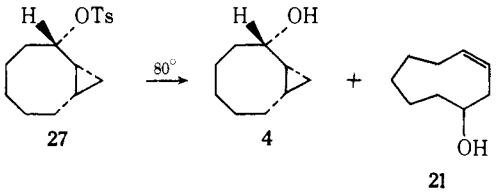
oxidized to **25** without purification. Addition of ethyl iodide to the enamine **26** gave an authentic sample of **25**[26] which gave a 2,4-dinitrophenylhydrazone which

(24) The general procedure used for the addition of dichloroketene was that of R. Montaigne and L. Ghosez, *Angew. Chem., Int. Ed. Engl.*, 7, 221 (1968).

(25) M. Hanack, H. Schneider-Bernlohr, H.-J. Schneider, R. Huttinger, and G. Wentrup, *Justus Liebigs Ann. Chem.*, 717, 41 (1968).

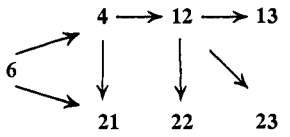
was identical in all respects with the same derivative of **25** derived from **22**.

In order to determine whether the complex mixture of products obtained in the solvolysis of **6** was a function of the reaction conditions, we prepared the tosylate of **4** (**27**) and solvolyzed it in buffered 70:30 dioxane–water at 80°. Under these conditions **27** gave only **4** and **21**




27 4 21

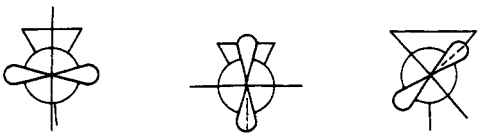
in a 3:2 ratio. As a result of this observation it became of interest to inspect the stability of the reaction products from **6** under the reaction conditions. In order to determine the sensitivity of these products to *p*-nitrobenzoic acid, no 2,6-lutidine was used in the control experiments. It was found that **13**, **21**, **22**, and **23** were stable to acidic conditions at 230° in 70:30 dioxane–water. However, under these same conditions **4** gave major amounts of **21** and **22** (in about a 2:1 ratio) and trace amounts of **12**, **13**, and **23**. The primary carbinol **12** was also unstable to the acidic conditions. It gave **22** and **13** in major amounts (about a 1.2:1 ratio) and small amounts of **23**. The formation of the six products, observed in the solvolysis of **6**, from the acid treatment of **4** at 230°, indicated that the carbonium ion(s) resulting from the ionization of **6** could serve as a precursor of all of the observed products under proper conditions. As noted schematically below, **6** gives **4** and **21** (and at high temperatures **12** and **13**) as primary products; **4** gives **21**, **12**, **13**, **22**, and




**23**; and **12** gives **13**, **22**, and **23**. From the data available we are not able to determine whether **4** yields **13**, **22**, and **23** directly or through the intermediacy of **12**. Since in principle protonation of **4** should give the same initial carbonium ion intermediate as **6** and **27** (with the exception of the degree of solvation) it seems probable that at the elevated temperatures of the solvolysis a mixture of carbonium ions may arise which leads to the product mixture observed from **6**. This concept was tested by monitoring the products from the solvolysis of **6** at 230° as a function of time. This study indicated that **4**, **12**, **13**, and **21** were primary products present at the very early stages of the solvolysis while **22** and **23** were arising from the rearrangement of **12** even under the buffered conditions. Thus it would seem that at 230° the thermally activated carbonium ion follows reaction paths which are not followed at 80°.

## Discussion

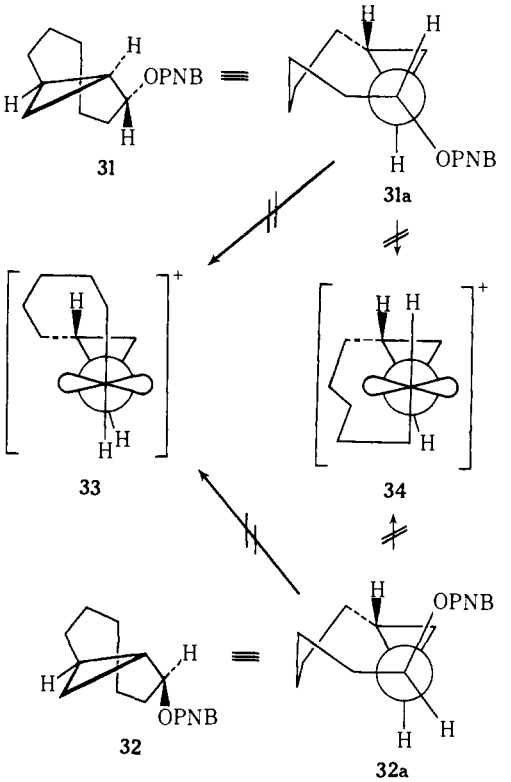
The major point of interest in connection with the solvolysis of **5** and **6** is the large rate difference of 12,000 between them. This rate difference would appear to be a function of the stereochemical relationship between the leaving *p*-nitrobenzoate anion and the neighboring cyclopropyl ring. Numerous groups have investigated the preferred structure of the cyclopropylcarbinyl cation.[27] Evidence has been presented relative to structures **28**, **29**, and **30** for the cyclopropylcarbinyl



28 29 30

cation. Recent findings have indicated that in freely rotating systems conformation **28** represents the preferred energy minimum,[28] while **29** is thought to be a relatively unfavorable arrangement. In **30** we are dealing with a type of homoallylic[5e,29] or bicyclobutonium[30] ion for which some evidence has been presented.[29,30] Presumably the process leading to the most stable ion will be the fastest, all other parameters being equal. This raises the question of why **5** should undergo ionization greater than $10^4$ times faster than **6** at 100° in dioxane–water.

If we consider **5** and **6** in terms of what should be their most stable conformations, **31** and **32**, respectively,




(27) For recent leading discussions, see (a) B. R. Ree and J. C. Martin, *ibid.*, **92**, 1660 (1970); (b) P. Schleyer and V. Buss, *ibid.*, **91**, 5880 (1969); (c) H. G. Richey, Jr. in "Carbonium Ions," Vol. 3, G. Olah and P. Schleyer, Ed., Interscience, New York, N. Y., 1969; (d) K. B. Wiberg, B. A. Andes, Jr., and A. J. Ashe in "Carbonium Ions," Vol. 3, G. Olah and P. Schleyer, Ed., Interscience, New York, N. Y., 1969; (e) M. Hanack and H. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967).

(28) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *J. Amer. Chem. Soc.*, **87**, 4533 (1965); C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 5123 (1965); P. Schleyer and G. W. Van Dine, *ibid.*, **88**, 2321 (1966); H. G. Richey, Jr., and J. M. Richey, *ibid.*, **88**, 4971 (1966); M. Vogel and J. D. Roberts, *ibid.*, **88**, 2262 (1966).

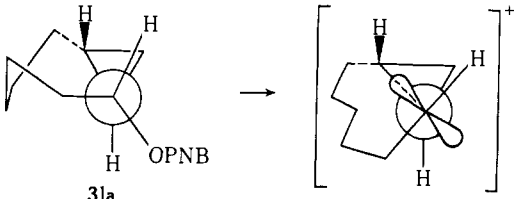
(29) M. Gasic, D. Whalen, B. Johnson, and S. Winstein, *ibid.*, **89**, 6382, 6384 (1967).

(30) W. B. Kover and J. D. Roberts, *ibid.*, **91**, 3687 (1969).

(26) G. Stork, A. Brizzolara, H. Landesman, J. Szmuszkovicz, and R. Terrell, *J. Amer. Chem. Soc.*, **85**, 207 (1963).

we see that they are very similar. As redrawn in terms of Newman projections, it can be seen that **31a** and **32a** differ only in the relationship of the leaving group to the neighboring cyclopropyl bonds. However, a major consequence of the trans-fused ring system can be seen from these projections when an attempt is made to convert either **31a** or **32a** into either of the "preferred" cyclopropylcarbinyl cations **33** or **34**. As can be readily seen from models, rotation to give **33** causes severe nonbonded interactions because the six carbon bridge must be stretched across the center of the cyclopropyl ring from one face of the ring to the opposite face. Models indicate that such a rotation is not feasible. Similarly, rotation to form the cation **34** is unreasonable because this would require unprecedented stretching of the six carbon bridge. Hence the formation of either of the preferred bisected cyclopropylcarbinyl cations from either **31** or **32** appears to be impossible. Since neither **31** nor **32** can form either **33** or **34**, the dramatic difference in their rates of solvolysis cannot be a function of whether one of these *p*-nitrobenzoates can form an ion of type **28** while the other cannot. This indicated that the rate difference must be due to some other factor.

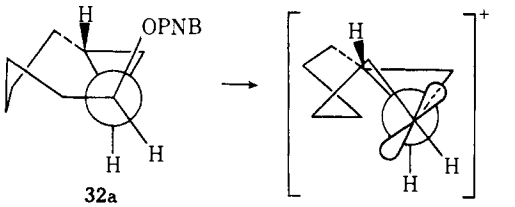
Inspection of **31a** and **32a** indicated that the major difference which could be rate influencing is the cis relationship of the *p*-nitrobenzoate to the nearest cyclopropyl bond in **32a** and the trans relationship of the *p*-nitrobenzoate to the nearest cyclopropyl bond in **31a**. In principle, **31a** could initially ionize to give **35** while **32a** could ionize to produce **36**. In both of these cases




**31a**




**35**



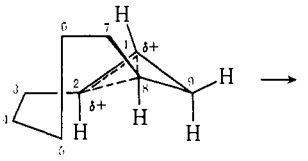

**32a**



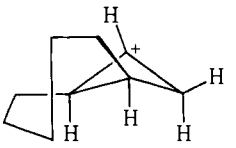

**36**

we are relying on neighboring group participation of the most parallel cyclopropyl bond. Models indicate that both **35** and **36** could exist, with **36** being somewhat more stable than **35**. However, since **31a** solvolyzes $>10^4$ times faster than **32a** it would appear that *significant neighboring cyclopropyl bond participation can only occur when the leaving group is trans to the participating bond, that is, when backside participation is allowed.* Thus we wish to suggest that **5** (**31a**) solvolyzes with participation of the cyclopropyl bond to give **35** while **6** (**32a**) solvolyzes without neighboring group participation to yield a classical carbonium ion. This indicates that neighboring cyclopropyl bond participation is accountable for a rate factor of greater than $10^4$ in the formation of a cyclopropylcarbinyl cation. On the basis of published reports[27a,b] it might be anticipated that this factor would exceed $10^4$. However, the actual transition state for the solvolysis of **5** may be even less ideal than that indicated by **31a**. This could account for the difference being only $10^4$.

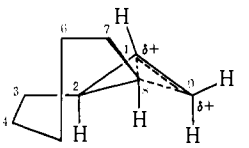
The products of the reaction are consistent with the discussion presented above. The ion **35** can be viewed in terms of the bicyclobutonium ion structure **35a**.




**35a**



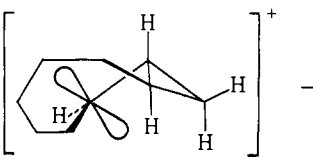

**37**



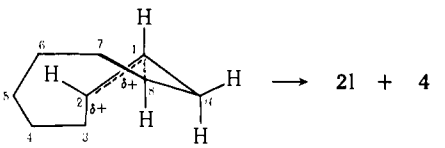

**38**

Attack of nucleophile at C-2 of **35a** would produce **3** with retention of stereochemistry, while attack at C-1 of **35a** would produce **13** with the observed stereochemistry. Interconversion of **35a** and **38** possibly *via* **37** would explain the origin of **12** since attack at C-9 of **38** would produce **12** with the observed stereochemistry while attack at C-1 of **38** would give **13**. In this manner all of the products from **5** and their associated stereochemistry are consistent with participation of the trans coplanar cyclopropyl bond in the rate-determining step.

The behavior of **6** was consistent with the lack of neighboring group participation in the rate-determining step. We feel that a classical ion was formed initially with the structure **39**. In this arrangement the p-




**39**



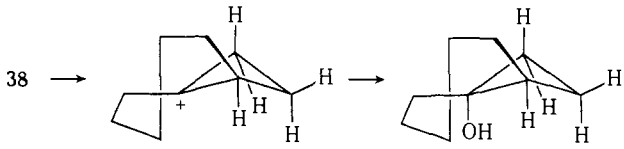

**40**

orbital can interact with the cyclopropyl ring in a variety of ways dependent on the mode of rotation about the carbon–carbon bonds of the cyclooctyl ring. Formation of the homoallylic cation **40** would readily explain the formation of major amounts of **21** *via* attack of the nucleophile at C-8 of **40**. Attack of nucleophile at C-2 would also be expected to occur to yield major amounts of **4** with retained stereochemistry. These expectations were confirmed by the isolation of **4** and **21**.

Rotation of the groups of **39** in the direction opposite to that which gave **40** would eventually produce ion **38**, which as noted above explains the presence of **12** and **13**. This accounted for all of the primary reaction products.

The formation of the two secondary products from **6** due to isomerization of the initially formed products

requires two different mechanistic paths. Attack of nucleophile at C-8 of **38** would produce **22** (with the vinyl group trans to the hydroxyl function). Both **4** and **12** should readily produce **38** on protonation followed by loss of water. The formation of **23** is somewhat more involved in that a hydride shift is required in order to produce the tertiary bridgehead cation which is a precursor of **23**. It seems most likely that this hydride shift may have occurred in ion **38** with the shift being from C-2 to C-1 to give **41**. Addition of nucleophilic solvent followed by loss of a proton would then give **23**.




In summary, the solvolyses of **5** and **6** appear to occur by different mechanisms. The solvolysis of **5** occurs with cyclopropyl participation while the solvolysis of the epimer **6** seems to occur with little or no accelerating influence on the neighboring cyclopropyl moiety. This concept appears to be supported by the thermodynamic parameters. The small enthalpy differences between **5** and **6** would be expected for rigid structures with similar ground-state energies. In the solvolysis of **6**, where the stabilizing influence of neighboring group participation is lacking, there is a greater dependence on solvation. Thus, **6** requires a more orderly solvent shell which is reflected in the large entropy differences between **5** and **6**. Backside participation by one of the cyclopropyl bonds seems to be ideal from the stereochemical point of view in the solvolysis of **5**. The fact that **5** solvolyzes faster than either **10** or **11** indicates that the rigid stereochemistry of **5** offers advantages in the ionization step, since the leaving group is always held trans antiparallel to the participating cyclopropyl bond in **5**.

## Experimental Section

Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Melting points and boiling points are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 137 Infracord as neat liquids, solutions in AR carbon tetrachloride, or powdered solids in potassium bromide disks. Near-infrared spectra were obtained on a Cary Model 14 recording spectrometer from 1 *M* solutions in AR carbon tetrachloride. Nuclear magnetic resonance spectra were obtained on Varian Associates A-60A and HA-100 spectrometers and reported $\tau$ units relative to tetramethylsilane ($\tau$ = 10.00) as the internal standard.

*trans*-**Cycloocten-3-ol** (**2**). Compound **2** was prepared by Marshall and DePuy's modification[9] of Whitham's procedure.[10]

*trans*-**2-Hydroxy-***trans*-**bicyclo[6.1.0]nonane** (**3**). The zinc–copper couple was prepared according to the procedure of LeGoff.[12] To a suspension of couple prepared from 40.4 g (0.62 mol) of zinc dust and 4.7 g (0.024 mol) of cupric acetate monohydrate in 450 ml of anhydrous ether was added several drops of methylene iodide. The reaction mixture was heated gently in an oil bath at 40°. The rest of the methylene iodide (total 149 g, 0.556 mol) and **2** (35 g, 0.278 mol) were added dropwise over a 30-min period during which reflux was maintained. The solution was permitted to reflux for an additional 0.5 hr, and cooled, and 100 ml of saturated ammonium chloride solution was added. The ether layer was decanted and the salts were washed with two 100-ml portions of ether. The combined ether extracts were washed with four 100-ml portions of saturated sodium carbonate and two 100-ml portions of saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solvent was removed on a rotary evaporator. The residue was added to 10 g of sodium methoxide in 150 ml of anhydrous methanol and permitted to stir at room temperature for 48 hr. Ether (500 ml) was added and the solution was washed with saturated sodium chloride solution (until neutral) and dried. The drying agent and the ether were removed and the residue was distilled *in vacuo* to give 24.3 g (62.5%) of **3** as a colorless, viscous liquid:[31] bp 95–96° (3.6 mm); $n^{26.4}$D 1.4952; near ir $\lambda_{max}$ 1.641 $\mu$ ($\epsilon$ 0.278); nmr ($CCl_4$) $\tau$ 10.05 (1 H, m, endo at $C_9$), 6.95 (1 H, m, $C_2$), 7.5 (1 H, s, hydroxyl), 8.05–9.67 (13 H, m, $C_1$, $C_3$–$C_8$). The alcohol was shown by glpc on a 10-ft 10% Carbowax 20M–KOH (4:1) on 60–80 Chromsorb W column at 150° to be >97% trans isomer. A small amount for an analytical sample was collected by preparative gas chromatography on a 6-ft 10% Carbowax 20M–KOH (4:1) on 45–60 Chromosorb W column at 150°.

*Anal.* Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 76.83; H, 11.45.

*trans*-**Bicyclo[6.1.0]nonan-2-one** (**1**). A solution of 1 g of **3** (0.007 mol) in 100 ml of acetone was cooled in an ice–water bath. Jones reagent[13] was added to the solution until the orange color of the reagent persisted. The solution was permitted to stir for 10 min at room temperature, and 15 ml of methanol was added. The reaction mixture was poured into 500 ml of water to dissolve the salts and the solution was extracted with three 150-ml portions of ether. The combined ether extracts were washed with three 100-ml portions of water and 150 ml of saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solution concentrated on a rotary evaporator. The residue was distilled *in vacuo* to give 0.667 g (67%) of **1**, bp 72–75° (2.3 mm). The ketone was shown by infrared analysis to be different than *cis*-bicyclo[6.1.0]-nonan-2-one.

*cis*-**2-Hydroxy-***trans*-**bicyclo[6.1.0]nonane** (**4**). A suspension of 0.34 g (0.009 mol) of lithium aluminum hydride in 50 ml of anhydrous ether was stirred while a solution of 1.24 g (0.009 mol) of **1** in 3 ml of ether was added dropwise over a 30-min period. The mixture was allowed to stir for 1 additional hr. A solution of 5% potassium hydroxide in water (1.36 g) was added dropwise, and the reaction mixture was stirred overnight. The solution was filtered and the ether was removed on a rotary evaporator. The residue was distilled at reduced pressure to give 1.05 g (85%) of a colorless liquid which solidified on standing at 5°: bp 79–81° (1.8 mm); $n^{25.8}$D 1.4938; near ir $\lambda_{max}$ 1.6415 $\mu$ ($\epsilon$ 0.227); nmr ($CCl_4$) 9.88 (1 H, m, endo at $C_9$), 7.72–9.72 (13 H, m, $C_1$ and $C_3$–$C_8$), 5.88 (1 H, m, $C_2$), 9.02 (1 H, s, hydroxyl). The alcohol was shown to be *ca.* 95% **4** by glpc on a 10-ft 10% Carbowax 20M–KOH (4:1) on 60–80 Chromosorb W column at 150°. A small portion of this alcohol was reoxidized to **3** to ensure that epimerization of the trans fusion had not occurred during reduction. An analytical sample was collected by preparative gas chromatography on a 6-ft 10% Carbowax 20M–KOH (4:1) on 45–60 Chromosorb W column at 150°.

*Anal.* Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.10; H, 11.40.

*trans*-**2-Hydroxy-***trans*-**bicyclo[6.1.0]nonane** *p*-**Nitrobenozate** (**5**). A solution of 2 g (0.0143 mol) of **3** in 30 ml of pyridine (dried and distilled from barium oxide) was cooled in an ice–water bath. A 10% excess of *p*-nitrobenzoyl chloride (3 g) was added over a 15-min period. The mixture was allowed to stand overnight at 5°, then poured into 150 ml of water and extracted with three 50-ml portions of chloroform. The combined chloroform extracts were washed with two 50-ml portions of 5% hydrochloric acid and three 50-ml portions of water, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the chloroform removed on a rotary evaporator to give 3.8 g (92%) of white, crystalline **5** which was recrystallized from hexane to a constant melting point of 85.5–87.0°; nmr ($CCl_4$) $\tau$ 5.5 (1 H, mult).

*Anal.* Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.54; H, 6.68; N, 4.88.

A small portion of **5** was reduced with lithium aluminum hydride, and the resultant alcohol was shown to be identical with **3** by comparison of infrared spectra.

*cis*-**2-Hydroxy-***trans*-**bicyclo[6.1.0]nonane** *p*-**Nitrobenzoate** (**6**). The preparation of **6** was identical with that described for **5**. When

(31) For purposes of simplicity the isomer with the hydroxyl function trans to the nearest cyclopropyl bond, relative to the cyclooctyl ring, is referred to as the trans isomer while the epimer is referred to as the cis isomer.

1.7 g of **4** was treated with 3 g of *p*-nitrobenzoyl chloride, 3.2 g (91%) of crude **6** was obtained. The crude product was recrystallized twice from hexane to give 1.8 g (57%) of white, crystalline **6**: mp 141.5–142.5°; nmr ($CCl_4$) $\tau$ 4.4 (**1** H, mult).

*Anal.* Calcd for $C_{16}H_{19}NO_4$: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.21; H, 6.70; N, 4.81.

A small portion of **6** was reduced with lithium aluminum hydride and the product was shown to be **4** by infrared spectral comparison.

**Kinetics. Reagents.** Reagent *p*-dioxane was purified by the method of Fieser.[32] The dioxane was accurately diluted with distilled water to form a 70% solution, and stored under nitrogen. Standard sodium hydroxide (*ca.* 0.006 *M*) used in titrating solvolysis aliquots was obtained by accurate dilution of a 0.0124 *M* solution which had been standardized against potassium acid phthalate primary standard using phenolphthalein as the indicator.

**Procedure.** All rates were obtained in 70% aqueous dioxane by titration of the liberated *p*-nitrobenzoic acid with sodium hydroxide to a pH 8 end point. Calculated infinity titers were used, and linear pseudo-first-order plots were obtained through greater than 65% reaction.

**Product Studies.** Compounds **5**, **6**, **10**, and **11** were solvolyzed for approximately 20 half-lives in the presence of excess 2,6-lutidine buffer, poured into water, and extracted with ether. The ether extracts were washed with 5% sodium bicarbonate, water, and saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The solvent was removed by distillation and the products separated by preparative glpc.

**Product Yields.** Yields were determined by glpc on a 10 ft × 3/8 in. 10% Carbowax 20M–KOH (4:1) on 60–80 Chromosorb W column. The products from **5**, **10**, and **11** were determined using 1-octanol as an internal standard, and those from **6** using 2-cyclohexylcyclohexanone as a standard. The products from **5**, **6**, and **11** were determined at 140°. Those from **10** were determined *via* temperature programming, with the starting alcohol *cis*-2-hydroxy-*cis*-bicyclo[6.1.0]nonane being determined at 140° and **21** being determined at 160°. The yields were determined directly by injection without work-up, after solvolysis for 10 half-lives.

**Solvolysis of *trans*-2-Hydroxy-*cis*-bicyclo[6.1.0]nonane *p*-Nitrobenzoate (11).** Compound **11** was solvolyzed for 20 half-lives at 185° and worked up as described above. The only product was isolated by preparative glpc[33] and shown to be the starting alcohol, *trans*-2-hydroxy-*cis*-bicyclo[6.1.0]nonane (92.8%), by comparison of ir and nmr spectra with those of an authentic sample. Only trace amounts of **13** were detected by glpc on three columns: 10-ft 10% Carbowax 20M–KOH (4:1) on 60–80 Chromosorb W at 140°, 3% FS1265 on 80–100 Chromosorb G at 80°, and 2% Hyprose SP80 on 80–100 Chromosorb G at 110°. Solvolysis of **11** for 1 half-life, recovery of the ester, and comparison of an ir spectrum and mixture melting point with authentic **12** ensured that the ester had not rearranged.

**Solvolysis of *cis*-2-Hydroxy-*cis*-bicyclo[6.1.0]nonane *p*-Nitrobenzoate (10).** Compound **10** was solvolyzed at 145° for 20 half-lives and worked up as usual. Two products were isolated by preparative glpc[33] and identified as starting alcohol (52%) and cyclononen-4-ol (**21**) (31%). Infrared and nmr spectra of both products were compared to those of authentic samples. Isolation of the ester after 1 half-life showed only **10** by ir spectral comparison and mixture melting point.

**Solvolysis of *trans*-2-Hydroxy-*trans*-bicyclo[6.1.0]nonane *p*-Nitrobenzoate (5).** Solvolysis of **5** for 20 half-lives at 110°, work-up, and glpc analysis on a 10-ft 10% Carbowax 20M–KOH (4:1) on 60–80 Chromosorb W column at 140° showed three products. Isolation by preparative gas chromatography[33] and comparison of ir and nmr spectra with authentic samples showed these to be **3** (77%), *exo*-8-hydroxymethyl-*cis*-bicyclo[5.1.0]octane (**12**) (10%), and *trans*-8-hydroxy-*cis*-bicyclo[5.2.0]nonane (**13**) (5%). The starting ester was isolated after a half-life and shown to be unrearranged by infrared spectral comparison and a mixture melting point with authentic **5**.

**Solvolysis of *cis*-2-Hydroxy-*trans*-bicyclo[6.1.0]nonane *p*-Nitrobenzoate (6).** Compound **6** was solvolyzed at 230° for 10 half-lives. Six products were isolated by preparative glpc;[33] five of these were identified by comparison of nmr and ir spectra with those of authentic samples. Two of the products were found to be secondary, arising from the primary products under the solvolysis conditions. The primary products obtained were **4** (9%), **21** (18%), **12** (17%), and **13** (10%). Secondary products obtained were 2-vinylcycloheptanol (**22**) (12%) and *cis*-bicyclo[5.2.0]nonan-1-ol (**23**) (10%). Compound **22** was identified by its distinctive nmr: ($CCl_4$) $\tau$ 4.51 (1 H, m, $\alpha$ proton of vinyl group), 4.98, 4.80 (2 H, t, q, $\beta$ protons of vinyl group), 6.55 (1 H, m, $C_1$), 8.2 (1 H, s, hydroxyl), 8.33 (11 H, m, $C_2$–$C_7$); and by converting it to 2-ethylcycloheptanone which was compared to an authentic sample. Compound **6** was recovered after 1 half-life, and an infrared spectrum and mixture melting point showed it to be unrearranged.

**Preparation of 27.** This tosylate was prepared by the method of Tanida, *et al.*[34] In a 50-ml, three-necked, round-bottomed flask equipped with a reflux condenser, gas inlet, rubber septum, and magnetic stirring bar, was placed 0.241 g (0.00172 mol) of **4** and 20 ml of anhydrous ether. The flask was thoroughly flushed with nitrogen and cooled to 5°. A slow stream of nitrogen was maintained as 1.05 ml (0.00189 mol) of a 15% solution of *n*-butyllithium in cyclohexane was introduced by means of a hypodermic syringe. The solution was stirred for 0.5 hr, and a solution of 0.363 g (0.00190 mol) of tosyl chloride in 5 ml of ether was added dropwise through a dropping funnel which replaced the rubber septum. The solution was allowed to stand overnight at 5°, and water was added. The aqueous layer was extracted with three 50-ml portions of ether and the combined ether layers were washed with 50 ml of 5% sodium bicarbonate, 50 ml of water, and 50 ml of saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solvent removed on a rotary evaporator. The oily residue was used without further purification. The purity of **27** was determined by ir and nmr spectroscopy. The absence of an OH stretch in the ir clearly indicated that all of the alcohol had reacted. There was no double bond stretch, or vinyl CH stretch in the ir and no vinyl protons in the nmr, indicating that the tosylate had not rearranged. The cyclopropyl protons were evident in the ir (CH stretch) and also in the nmr ($\tau$ 9.62). A small amount of tosyl chloride was evident in the nmr.

**Solvolysis of 27.** A small amount of **27** was solvolyzed in 70% aqueous dioxane at 230° for 0.5 hr using lutidine as a buffer. The solution was added to water and extracted with ether. The ether extracts were injected directly onto a vpc and analyzed on a 10% Carbowax 20M–KOH (4:1) on 60–80 Chromosorb W column at 170°. The major product was **21** (*ca.* 72%). In addition, *ca.* 13% **22**, 9% **4**, 3% **13**, 2% **12**, and a trace amount of **23** were observed.[35]

When solvolysis was carried out under the same conditions at 80° for 10 hr, only **4** and **21** were observed in *ca.* 60 and 40% yields, respectively.

**Solvolysis Products. Cyclononen-4-ol (21).** Cyclononen-4-ol was prepared by the lithium aluminum hydride reduction of a crude sample of cyclononen-4-one.[36] A mixture of 0.5 g of cyclononen-3-one[37] and 30 ml of a *ca.* 1.5% solution of *p*-toluenesulfonic acid in benzene was refluxed in a dry atmosphere for 24 hr. The solution was cooled and poured onto an aqueous sodium bicarbonate solution, and the benzene layer was recovered and dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the solution concentrated by distillation to give a crude sample of the isomerized cyclononen-4-one. This isomerized ketone had an infrared absorption (neat) at 5.86 $\mu$ compared to 6.03 $\mu$ for cyclononen-3-one.

The crude ketone was added dropwise to a well-stirred solution of 150 mg of lithium aluminum hydride in 50 ml of anhydrous ether. The solution was stirred for 2 hr and then hydrolyzed by the dropwise addition of 600 mg of a 10% aqueous sodium hydroxide solution. After stirring overnight, the solution was filtered to remove the precipitated salts and the filtrate was concentrated by careful distillation of the ether. The residue was subjected to molecular distillation to give 50 mg of cyclononen-4-ol. A comparison of vpc retention times on a 10% Carbowax 20M–KOH (4:1) on 60–80 Chromosorb W column at 160° showed less than 1% of cyclononen-3-ol was present.

***exo*-8-Hydroxymethyl-*cis*-bicyclo[5.1.0]octane (12).** Compound **12** was prepared according to the procedure of Kirmse and Pook.[22]

(32) L. F. Fieser, "Experiments in Organic Chemistry," 3rd ed, Heath, Boston, Mass., 1965, p 284.

(33) A 6 ft × 3/8 in. 10% Carbowax 20M–KOH (4:1) on 45–60 Chromosorb W column was used.

(34) H. Tanida, Y. Hata, S. Ikegami, and H. Ishitobi, *J. Amer. Chem. Soc.*, **89**, 2928 (1967).

(35) All products observed from the solvolysis of **6** and **27** were stable at 230° in 70:30 dioxane–water in the absence of acid.

(36) N. Heap and G. H. Whitham, *J. Chem. Soc. B*, 164 (1966).

(37) We wish to thank Dr. G. Mehta for a sample of cyclononen-3-one.

This material was contaminated with *ca.* 15% of the epimeric endo alcohol. The mixture of alcohols was used without purification.

***cis*-Bicyclo[5.1.0]octene-*exo*-8-aldehyde (14).** Aldehyde **14** was prepared by Collins oxidation[23] of the mixture of 8-hydroxymethyl-*cis*-bicyclo[5.1.0]octanes. A solution of 14 g of the mixture of alcohols, 3100 ml of methylene chloride, and 155 g of Collins reagent[23] was stirred at room temperature for 5 hr. The brownish black solution was filtered and the methylene chloride removed on the flash evaporator. The residue was distilled *in vacuo* to give 10.1 g (73%) of **14**, bp 95–100° (15 mm), contaminated with *ca.* 15% of the epimeric aldehyde. This mixture was used in the next step.

**Tosylhydrazone of *cis*-Bicyclo[5.1.0]octane-*exo*-8-aldehyde (15).** The tosylhydrazone **15** was prepared by a modification of the procedure of Kirmse and Pook.[22] A solution of 6.9 g of **14**, 9.3 g of tosylhydrazine, 90 ml of methanol, 30 ml of water, 15 ml of acetic acid, and 5 drops of concentrated hydrochloric acid was stirred at room temperature for 1 hr. The solution was cooled in an ice–water bath and water was added dropwise to induce precipitation. The solution was stirred for 1 additional hr, and the white solid was filtered off and washed with cold methanol. The solid was dried in a vacuum oven to give 12.4 g (81%) of **15**, mp 88–91°, which was shown to contain a small amount of aldehyde, **14**, by ir spectroscopy.

***cis*-Bicyclo[5.2.0]non-8-ene (16).** The bicyclic olefin **16** was prepared by pyrolysis of the dry salt of the tosylhydrazone, **15**. A solution of 10 g of **15**, 500 ml of ether, and 1.6 g of sodium hydride was stirred for 24 hr. The white precipitate was filtered, washed well with ether, and dried in a vacuum oven. The dried sodium salt was pyrolyzed at 140–160° at a pressure of 3 mm and the volatile liquid, which was passed through a 5-in. Vigreux column, was collected in a trap cooled in a Dry Ice–isopropyl alcohol bath. In this manner, 1.28 g of liquid was collected which was shown by vpc analysis on a 10% SE-30 on 80–100 Diatoport S column at 60° to consist of *ca.* 80% **16**[12] and 20% cycloheptene (pyrolysis of **15** is reported to give cycloheptene from a fragmentation reaction which also produced acetylene[12]).

***trans*-8-Hydroxy-*cis*-bicyclo[5.2.0]nonane (13).** A 100-ml three-necked round-bottomed flask, flushed with nitrogen and cooled in an ice–water bath, was charged with 1 g of the olefin mixture of **16** and cycloheptene and 10 ml of dry tetrahydrofuran. To this mixture was added 19.2 ml of a 1.1 *M* diborane in tetrahydrofuran solution. After stirring at room temperature for 0.5 hr, the excess diborane was decomposed by the careful addition of water. The organoborane was oxidized at 50° by the addition of 12 ml of 3 *N* sodium hydroxide, followed by the dropwise addition of 12 ml of 30% hydrogen peroxide. After stirring for 1 hr at room temperature, 37.5 g of potassium carbonate was added, the organic layer was separated, and the aqueous phase was extracted twice with 15-ml portions of tetrahydrofuran. The combined organic extracts were dried over anhydrous magnesium sulfate, the drying agent was removed by filtration, and the solvent was removed by distillation to give 0.87 g of a crude mixture of alcohols estimated by vpc on a 2% Hyprose on 80–100 Chromosorb G column at 160° to consist of *ca.* 70% **13**, *ca.* 10% *cis*-bicyclo[5.2.0]nonan-*endo*-8-ol (**17**), and *ca.* 20% cycloheptanol.

An analytical sample of **13** was collected by preparative vpc on a 20 ft × 0.25 in. Hyprose on 60–80 Chromosorb G DMCS column at 150°, $n^{24.5}$D 1.4855.

*Anal.* Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.05; H, 11.48.

**9,9-Dichloro-*cis*-bicyclo[5.2.0]nonan-8-one (19).**[24] A mixture of 15 g of dichloroacetyl chloride, 15 g of cycloheptene, and 200 ml of hexane was stirred in a 1000-ml three-necked round-bottomed flask at room temperature under a nitrogen atmosphere. A solution of 10 g of dry triethylamine in 200 ml of hexane was added dropwise to this mixture. After stirring overnight, the reaction mixture was filtered, and the filtrate was poured onto an ice–water mixture. The organic phase was separated and washed with cold solutions of water, dilute hydrochloric acid, water, and saturated sodium chloride solution. The hexane phase was dried over anhydrous magnesium sulfate, and the drying agent was removed by filtration. The hexane was removed on the rotary evaporator and the residue distilled *in vacuo* to give 8.8 g (42%) of **19**, as a yellow liquid, bp 80–100° (0.1 mm).

An analytical sample of **19** was collected by preparative vpc on a 1% FS 1265 on 80–100 Chromosorb G column at 120°, $n^{24.5}$D 1.5088.

*Anal.* Calcd for $C_9H_{12}OCl_2$: C, 52.20; H, 5.84. Found: C, 52.35; H, 5.90.

Compound **19** showed a strong absorption band at 5.56 μ indicative of an α,α-dichlorocyclobutanone.

***cis*-Bicyclo[5.2.0]nonan-8-one (20).** To a stirred mixture of 5.66 g of crude **19**, 150 ml of cyclohexane, and a catalytic amount of azobisisobutyronitrile under a nitrogen atmosphere was slowly added 16.4 g of tri-*n*-butyltin hydride. The solution was refluxed for 8 hr, the cyclohexane was removed by distillation, and the residue was distilled *in vacuo* to give 2.23 g (60%) of **20**, bp 55–60° (0.8 mm). Compound **20** had an infrared absorption (neat) at 5.62 μ characteristic of a cyclobutanone. In addition, the remainder of the ir and nmr data for **20** agreed well with the published data of Winstein and coworkers on this compound.[5e]

An analytical sample of **20** was collected by preparative vpc on a 10-ft 10% Carbowax 20M–KOH (4:1) on 60–80 Chromosorb W column at 140°; $n^{24.5}$D 1.4788.

*Anal.* Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.23; H, 10.27.

In addition, compound **20** was found to be identical in all respects with the ketone obtained by Jones oxidation[13] of alcohol **13**.

***endo*-8-Hydroxy-*cis*-bicyclo[5.2.0]nonane (17) from Lithium Aluminum Hydride Reduction of 20.** Compound **20** (0.10 g, 0.0007 mol) in anhydrous ether was added slowly to a suspension of 0.05 g (0.001 mol) of lithium aluminum hydride in ether. The mixture was permitted to stir for 30 min, then 0.20 g of 5% potassium hydroxide solution was added dropwise and allowed to stir overnight. Filtration and removal of solvent on a rotary evaporator gave 86 mg (85.1%) of a mixture of **17** and **13**, which were shown to be in the ratio *ca.* 2:1 by glpc analysis on a 2% Hyprose SP 80 on 80–100 Chromosorb G column at 100°.

**1-Morpholinocycloheptene (26).** Compound **26** was prepared according to the procedure of Stork.[26] Cycloheptanone (29.4 g, 0.263 mol), morpholine (35 g, 0.40 mol), and 0.5 g of *p*-toluenesulfonic acid in 100 ml of toluene were heated to reflux in a flask equipped with a Dean–Stark trap to remove water as it formed (72 hr). The excess toluene and morpholine were removed by distillation, and the product distilled *in vacuo* to give 35.7 g (75%) of **26**: bp 133–134° (17 mm); ir 1650 $cm^{-1}$ (C=C), no C=O at 1710 $cm^{-1}$; nmr ($CCl_4$) τ 5.20 (1 H, t, vinyl proton), 6.30 (4 H, m, $CH_2$ next to O), 7.38 (4 H, m, $CH_2$ next to N), 7.90 (4 H, m, allylic protons on $C_3$, $C_7$), 8.42 (6 H, m, $C_4$–$C_6$).

**2-Ethylcycloheptanone (25).** Ketone **25** was prepared by refluxing 35.7 g (0.197 mol) of **26** and 40 g (0.256 mol) of ethyl iodide in 250 ml of toluene for 24 hr. Water (50 ml) was added slowly and the reaction mixture refluxed overnight. A solution of 10% sulfuric acid (50 ml) was added and the aqueous layer was extracted with ether. Ether extracts were washed with 10% sodium carbonate and water, then dried over anhydrous magnesium sulfate. The drying agent was removed by filtration, and the solution was distilled to give cycloheptanone and **25** in the ratio 9:1. The two were separated by preparative glpc[33] at 130°. The major product had an ir identical with cycloheptanone. The minor product was converted to its 2,4-dinitrophenylhydrazone derivative and the bright orange needles recrystallized from 95% ethanol, mp 116–117° (lit. 116°[38]).

**Hydrogenation of 22.** A 20-ml round-bottomed flask was flushed thoroughly with nitrogen and charged with 8 mg of 5% palladium-on-carbon catalyst and 10 ml of anhydrous ether. The flask was thoroughly flushed with hydrogen, 30 mg of 2-vinylcycloheptanol (**22**) was added, and the flask stoppered with a rubber septum. Another flask was flushed with hydrogen, and 15 ml of hydrogen was syringe transferred to the reaction flask to create a positive hydrogen pressure. The reaction mixture was stirred for 4 hr and another 5 ml of hydrogen was added. The reaction mixture was permitted to stir overnight, the solution was filtered, and the solvent was removed on a rotary evaporator. The product, **24** (25 mg, 84%), was subjected to Jones oxidation without further purification.

**Jones Oxidation of 2-Ethylcycloheptanol.** The same procedure as previously described for oxidation of **3** was used. The product obtained had an infrared spectrum identical with that of authentic **25**. The ketone was also converted to its 2,4-dinitrophenylhydrazone derivative (mp 115.5–116.5°). A mixture melting point with the material prepared above showed no depression.

***cis*-Bicyclo[5.2.0]nonan-1-ol (23).**[25] A 0.63-g sample of 1-cycloheptenylethylamine prepared according to the procedure of Hanack[25]

(38) J. Rouzaud, G. Cauquil, and L. Giral, *Bull. Soc. Chim. Fr.*, 2030 (1965).

was dissolved in 25 ml of 15% perchloric acid which had been brought to pH 2.5 by careful addition of 2 *N* sodium hydroxide while cooling the solution in an ice bath. An aqueous solution of 0.63 g of sodium nitrite in 10 ml of water was added slowly, maintaining the pH between 2.3 and 2.7. The solution was then heated to 60° for 6 hr and cooled, and saturated sodium chloride solution was added. The product was extracted with ether, washed with water, and dried. Filtration to remove the drying agent, and removal of the solvent on a rotary evaporator followed by preparative glpc of a small amount of the reaction mixture on a 6-ft 15% Carbowax 1500–3% KOH on 60–80 Chromosorb G column at 130° gave **23**: nmr ($CCl_4$) $\tau$ 7.6–8.9 (broad envelope of ring protons), no proton on the carbon bearing the hydroxyl group, 8.6 (s, hydroxyl); ir 3510 (OH stretch), 1125 $cm^{-1}$ (tertiary CO stretch).

**Acid-Catalyzed Rearrangements of Products of Solvolysis of 6.** The products of solvolysis of **6** were subjected to nonbuffered solvolysis conditions to determine which were stable. The alcohols were each placed in a sealed tube in a solution of 0.025 *M* *p*-nitrobenzoic acid in 70% aqueous dioxane and heated at 230° [39] for 2 hr. The solutions were analyzed directly by glpc on a 10% Carbowax 20M–KOH on 60–80 Chromosorb G column at 160°, and retention times were compared to authentic samples. Compounds **21**, **13**, **22**, and **23** were found to be stable under these conditions. Compound **4** rearranged to give **21** and **22** as major products (*ca.* 2:1), a small amount of **13**, and traces of **12** and **23**. Compound **12** rearranged to give **22** and **13** as major products (*ca.* 1.2:1) and a small amount of **23**.

**Acknowledgment.** We are indebted to the National Science Foundation for a grant which supported this investigation.

(39) A batch of Dow-Corning 210-H Fluid was used.

# 1,2-, 1,4-, 1,5-, and 1,6-Halogen Participation in the Trifluoroacetolysis of Primary Alkyl Nosylates

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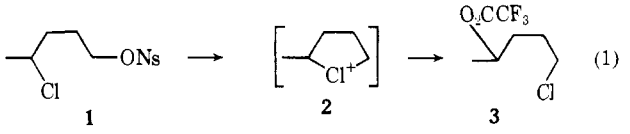
**Abstract:** The trifluoroacetolyses of the following *p*-nitrobenzenesulfonates were studied: 2-chloro-1-propyl, 3-chloro-1-butyl, 4-chloro-1-pentyl, 5-chloro-1-hexyl, 6-chloro-1-heptyl, and 5-bromo-1-hexyl. Trifluoroacetolysis of 2-chloro-1-propyl and 4-chloro-1-pentyl nosylates gave substantially quantitative 1,2- and 1,4-halogen shifts. The extent of halogen shift was reduced to 90% for 5-chloro-1-hexyl nosylate and ~17% for 6-chloro-1-heptyl nosylate. Rate accelerations owing to chlorine participation by factors of 2000, 760, and 7.1 were estimated from analysis of measured rates for 2-, 4-, and 5-chloro-1-alkyl nosylates, respectively. Halonium ion intermediates having three-, five-, six-, and seven-membered rings are postulated to explain the halogen shifts and rate accelerations observed.

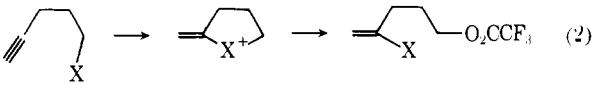
In a preliminary communication we have reported[1] that trifluoroacetolysis of the primary nosylate (*p*-nitrobenzenesulfonate) **1** leads (presumably *via* halonium ion **2**) to the product of 1,4-halogen shift **3** to the extent of 99.5% (eq 1). The first 1,5-halogen shifts also



(1)

were reported in the analogous reactions of the homologs 5-chloro- and 5-bromo-1-hexyl nosylate. Based on these results, it seemed probable that the combination of a primary leaving group, a secondary halide participating group, and a weakly nucleophilic solvent constitutes the most favorable system for the observation of halogen participation yet found. Accordingly, we have extended the study, as reported here, to include determinations of reaction rates and additional halogen shift reactions. The results uphold the promise shown in the preliminary studies.

Previous studies from our laboratories established that halogen participation of the type mentioned above is not uncommon. Reaction of 5-halo-1-alkynes with trifluoroacetic acid, for example, gave predominantly halogen-shifted products (eq 2).[2] Alkenes showed evidence for an extent of 1,4-halogen participation in reaction with trifluoroacetic acid similar to that in alkynes,[3]



(2)

whereas cyclopropane ring openings in trifluoroacetic acid showed less participation.[4] On the other hand, solvolyses of ω-halo secondary tosylates showed more participation than the comparable reactions of alkynes.[5] These secondary tosylate–primary chloride solvolyses, which are closely related to the reactions to be reported in this paper, resulted in no halogen shifts, however. 5-Chloro-2-pentyl tosylate, for example, was postulated (from rate evidence) to react predominantly *via* the ion **2** (eq 1), which opened to the unshifted product **3**. Furthermore, the rate accelerations owing to 1,4-halogen participation in these tosylate reactions were evident only if substantial allowances for inductive effects in the nonparticipation (normal solvolysis) reaction

(1) (a) P. E. Peterson and J. F. Coffey, *Tetrahedron Lett.*, 3131 (1968); (b) *cf.* W. S. Traynovsky, G. L. Smyser, and M. D. Doyle, *ibid.*, 3127 (1968).

(2) P. E. Peterson, R. J. Bopp, and M. M. Ajo, *J. Amer. Chem. Soc.*, **92**, 2834 (1970), and earlier references cited therein.

(3) P. E. Peterson, C. Casey, E. V. P. Tao, A. Agtarap, and G. Thompson, *ibid.*, **87**, 5163 (1965).

(4) P. E. Peterson and G. W. Thompson, *J. Org. Chem.*, **33**, 968 (1968).

(5) P. E. Peterson, R. J. Bopp, D. M. Chevli, E. L. Curran, D. E. Dillard, and R. J. Kamat, *J. Amer. Chem. Soc.*, **89**, 5902 (1967).