0.92 (d, 3, J = 7.0 cps, Me of *i*-Pr), 1.22 (s, 3, Me), 3.60 (m, 2, oxymethylene).

Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90. Found: C, 70.63; H, 11.92.

Acknowledgment. The authors are indebted to Eli Lilly and Co. and the National Science Foundation for support of this investigation.

Solvolysis of Bicyclo[4.2.0]octane-1-methyl *p*-Toluenesulfonate[1a]

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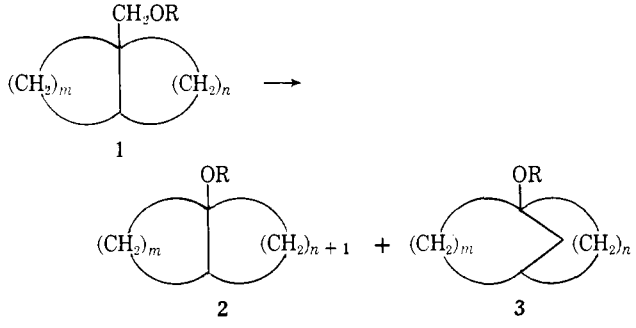
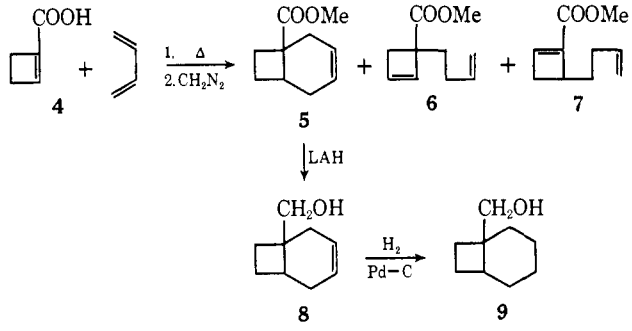
Abstract: Bicyclo[4.2.0]octane-1-methanol (**9**) was synthesized in a three-step reaction sequence from the Diels–Alder adduct of 1-cyclobutene-1-carboxylic acid (**4**) and butadiene *via* methyl bicyclo[4.2.0]oct-3-ene-1-carboxylate (**5**) and bicyclo[4.2.0]oct-3-ene-1-methanol (**8**). The *p*-toluenesulfonate ester **10** underwent solvolysis in buffered acetic acid to yield 90% of 1-bicyclo[4.2.1]nonyl acetate (**12c**) and 10% of 1-bicyclo[4.2.1]nonyl *p*-toluenesulfonate (**12d**). The rate of the reaction was determined at 41.6 and 60.6° and the calculated rate at 100° is 1.0×10^4 faster than the rate of neopentyl *p*-toluenesulfonate. The effects of conformation, ring size, and strain on the course and rate of these neopentyl-type rearrangements are discussed.

Recently a correlation between hydrocarbon strain release and solvolysis rate was reported for a series of bicyclo[*m*.*n*.0]alkane-1-methanols (**1**) as being indicative of alkyl participation in neopentyl rearrangements.[2] As *m* and *n* get smaller, the rearrangement rate increases and the type of product changes from **2** to **3**. The effects of conformation, ring size, and strain on the course, as well as the rate, of these neopentyl-type rearrangements continues to be of interest.



Bicyclo[4.2.0]octane-1-methanol (**9**), an interesting system in its own right, is of particular interest here since it provides an additional check for the strain release–rate correlation and since it is a neopentyl system in which the maximum hydrocarbon strain release should give expansion of the smaller ring leading to **2** (m = 4, n = 3) rather than expansion of both rings simultaneously (bridging) leading to **3** (m = 4, n = 2).

Syntheses. 1-Cyclobutene-1-carboxylic acid (**4**) was allowed to react with butadiene under pressure at 120° and the resulting acidic products were esterified. Methyl bicyclo[4.2.0]oct-3-ene-1-carboxylate (**5**) was obtained by spinning-band distillation or vpc. Two minor components (4% acidic fraction) were most likely "ene" reaction products[3] of butadiene and **4** since



(1) they were isomeric with the major product, (2) their spectra match the suggested structural assignments; in particular, they had two sets of olefinic protons in the nmr whose patterns were consistent with the assignment, and (3) hydroboration and Jones oxidation of the mixture of alcohols indicated that the cyclobutane ring was still intact and that it contained one of the double bonds, since cyclobutanone derivatives were obtained ($\nu_{C=O}^{CCl_4}$ 1780 cm^{-1}). These two minor components were formed in approximately equal amounts. The minor component whose vpc retention time was less than that of **5** was assigned structure **6**; the minor component of longer retention time (almost twice as long as **5**) was assigned structure **7**. The infrared spectrum of the conjugated ester **7** showed a 1705-cm^{-1} ester band, and its nmr spectrum showed only one cyclobutenyl hydrogen. The unconjugated ester **6**, however, had a vpc retention time similar to that of **5**, its infrared spectrum showed a normal, unconjugated ester band at 1735 cm^{-1}, and its nmr spectrum showed two cyclobutenyl hydrogens.

The ester **5** was reduced with lithium aluminum hydride to bicyclo[4.2.0]oct-3-ene-1-methanol (**8**) and **8** was catalytically hydrogenated to bicyclo[4.2.0]-octane-1-methanol (**9**). The *p*-toluenesulfonate ester of **9** was prepared from *p*-toluenesulfonyl chloride in pyridine and **9**.

(1) (a) This work was supported in part by Grant GP-3890 from the National Science Foundation; (b) National Institutes of Health Predoctoral Fellow, 1966–1968.

(2) W. G. Dauben, J. L. Chitwood, and K. V. Scherer, Jr., *J. Amer. Chem. Soc.*, 90, 1014 (1968).

(3) For a recent review see: J. A. Berson, R. G. Wall, and H. D. Perlmutter, *ibid.*, 88, 187 (1966); and the references therein.

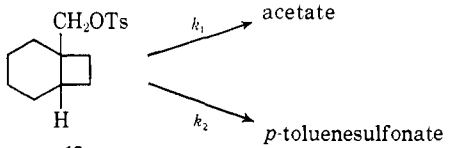
Solvolysis. The bicyclo[4.2.0]octane-1-methyl *p*-toluenesulfonate (**10**) used for this study was analytically pure and was prepared from alcohol **9** which was also analytically pure. Kinetic and product determinations were carried out in acetic acid buffered with sodium acetate. In order to determine an approximate half-life, the rearrangement rate at 57.0–57.5° was monitored *via* nmr by observing the decline of the singlet at δ 3.7 relative to the aromatic signal centered at δ 7.4 (as determined by electronic integration on a Varian A-60 instrument). Four points were taken; the half-life estimated from these points was 33.5 min or $k_{57°} = 3.4 \times 10^{-4}$ sec^{-1}.

Table I. First-Order Rate Constants[a] in Buffered Acetic Acid[b]

Substrate[c]	Temp,[d] °C	$k_1 \times 10^4$, sec^{-1}
Bicyclo[4.2.0]octane-1-methyl OTs	41.55	0.38 ± 0.01[e]
	60.59	3.74 ± 0.04[e]
	100.0	217 (calcd)

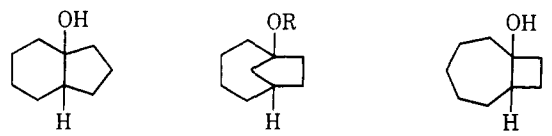
[a] Determined from two runs at each temperature. [b] Buffered with 15% molar excess of sodium acetate. [c] 0.010 *M*. [d] ±0.03. [e] Standard deviation.

The solvolysis rates given in Table I were determined more precisely and at two different temperatures by the automatic, potentiometric titration of free sodium acetate remaining. The infinity point for these titrations was 90.4% of theoretical, indicating 9.6% of the arrangement had occurred with internal return. The total rearrangement rate ($k_1 + k_2$) given in Table I was determined from a plot of ln $(V_t - V_\infty/V_0 - V_\infty)$ against time.[4]



10

There are three possible structures for the Wagner-Meerwin rearrangement product from the acetolysis of **10** (followed by reduction with lithium aluminum hydride); they are **11**, **12a**, and **13**. Structure **13** is unlikely since the total strain energy of the system would be increased during the rearrangement, but structures **11** and **12a** both release strain energy during



11 **12a**, R = H; **b**, R = Cl; **c**, R = OAc; **d**, R = OTs **13**

the rearrangement. The infrared spectrum of the solvolysis product was different from that of **11**.[5] Therefore, it seemed likely that the alcohol obtained from the solvolysis was **12a** and to check this assignment, the alcohol from the solvolysis was treated with phosphorus oxychloride in pyridine. Under these mild E2 conditions, both 1-bicyclo[4.4.1]undecanol and 1-bicyclo[4.3.1]decanol eliminate while 1-bicyclo[3.3.1]-nonanol gives only unrearranged chloride. One would, therefore, expect **11** and **13** to give olefin and **12a** to give chloride. The alcohol from the solvolysis of **10** gave only chloride **12b**.

It was obvious from the ir (1190, 1175 cm^{-1}) and nmr (doublet of doublets centered at δ 7.4 and the absence of a singlet at δ 3.7) spectra of the solvolysis mixture, as well as from the kinetic studies above, that 9.6% of the rearrangement occurred with internal return to the *p*-toluenesulfonate ester. To ascertain the identity of this rearranged *p*-toluenesulfonate ester, the solvolysis mixture was reduced with lithium metal in liquid ammonia. Under these conditions the *p*-toluenesulfonate ester is reduced more rapidly than the acetate ester.[6] The alcohol obtained from this reduction was identical by ir (no other isomers present by vpc) with the alcohol **12a** obtained from the lithium aluminum hydride reduction of the solvolysis mixture (where only the acetates are converted to alcohols). Thus, the rearrangement proceeded exclusively to the bicyclo[4.2.1]nonyl system giving 90% 1-bicyclo[4.2.1]-nonyl acetate (**12c**) and 10% internal return to 1-bicyclo[4.2.1]nonyl *p*-toluenesulfonate (**12d**).

Discussion

The results of the present study of the solvolysis of *cis*-bicyclo[4.2.0]octane-1-methyl *p*-toluenesulfonate (**10**) when compared with the solvolytic chemistry of other *cis*-fused bicyclic neopentyl systems are of interest from both the magnitude of the rate and from the nature of the products. Considering the rate first, it has been shown earlier[2] that a least-squares plot of the log of the relative rates of various bicyclic neopentyl systems *vs.* the estimated potential strain release is linear with a slope of 0.145 kcal/mol as shown in Figure 1. As in the earlier studies, the strain release in going from the bicyclo[4.2.0]octane to the bicyclo-[4.2.1]nonane ring system was estimated as a composite of the strain energies of the component rings. Using this value of 13.6 kcal/mol and the relative rate of 1.0×10^4, the point for the bicyclo-[4.2.0]octane-1-methyl system falls on the general line shown in Figure 1. It is appreciated that this correlation with strain release as measured by the products is inferior to knowing the strain release actually present in the activated complex. The correlation, however, in its present form when coupled with the dramatic rate enhancement observed for the more strained compounds in this series strongly suggests anchimeric assistance with a portion of the hydrocarbon strain release being felt in the activated complex.

An equally interesting result of this whole study is the finding that as the size of the rings of the bicyclo[*m.n.*0]-alkane system decrease, both the rate of solvolysis and the amount of bridging to yield bicyclo[*m.n.*1]alkane products increases markedly. The increasing difficulty of forming a relatively planar carbonium ion in a bicyclo[*m.n.*1]alkane system as the ring sizes decrease is

(4) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 171.
(5) R. A. Flath, Dissertation, University of California, Berkeley, Calif., 1963.
(6) H. Smith, "Organic Reactions in Liquid Ammonia," Interscience Publishers, New York, N. Y., 1963, p 181.

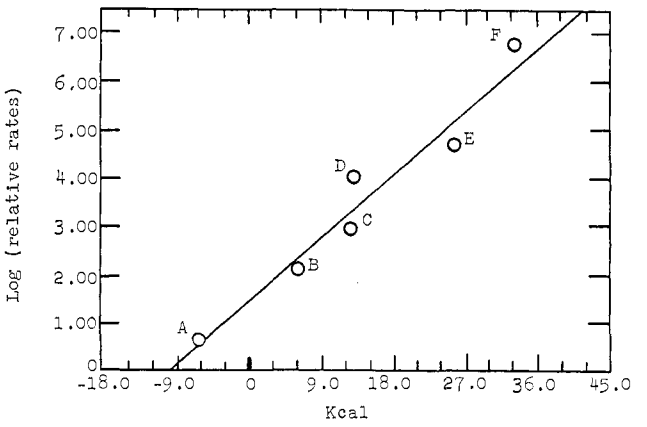


Figure 1. Plot of the log of the experimental relative rate constants for *p*-toluenesulfonate acetolysis plotted against the calculated hydrocarbon–hydrocarbon strain differences for the bicyclo[*m.n.*0]alkane-1-methyl systems: A, *cis*-bicyclo[4.4.0]decane-1-methyl; B, *cis*-bicyclo[4.3.0]nonane-1-methyl; C, *cis*-bicyclo[3.3.0]decane-1-methyl; D, *cis*-bicyclo[4.2.0]octane-1-methyl; E, *cis*-bicyclo[3.2.0]-heptane-1-methyl; F, *cis*-bicyclo[2.2.0]hexane-1-methyl.

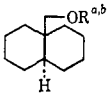
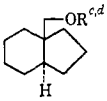
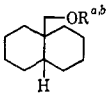
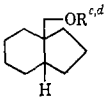
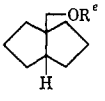
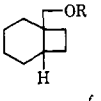
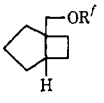
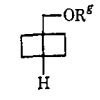
not reflected in the solvolysis rates. Rather, the increasing drive to release ring strain results in increasing rate enhancement with a greater percentage of the products arising through participation by the common bond of the fused ring system (the zero-bridged bond). This insensitivity to the stability of the cation formed suggests that the geometry of the transition state is nearer that of starting material (or some intermediate species) than that of the products in the rapidly reacting systems.

In order to assess the importance of the above suggestion, it must be appreciated that the bicyclo[*m.n.*0]-alkane-1-methyl series (**1**) has two rearrangement pathways available, expansion to another bicyclo[*m.n.*0]-alkane system **2** and bridging to a bicyclo[*m.n.*1]alkane (**3**). If *m* and *n* are different, there are two possible compounds of the general form **2**; however, it was found that in all cases the smaller ring is involved in every rearrangement. The extent to which these rearrangement pathways are followed for the ester solvolysis of the bicyclo[*m.n.*0]alkane-1-methyl series is presented in Table II. The pathways for the deamination of amines of this same series are summarized in Table III.

Before evaluating the features controlling the migratory pathway, it was necessary to establish that the products observed were derived from the first-formed carbonium ion intermediate, that is, no secondary rearrangements were occurring. The stability of the first-formed product was particularly of concern with the ester solvolysis of the first two compounds in this series since, in contrast with the other compounds in this series and in contrast with their own deamination results, they did not give predominately bridged products. Both the mesylate and the olefin of 1-bicyclo-[4.4.1]undecene system give unrearranged material under the conditions of the solvolysis. In fact, all attempts to equilibrate the two possible bicyclic products from the decalylcarbinyl system failed. Similarly, derivatives of the bicyclo[3.3.1]nonane system[7,8] and the bicyclo[4.3.1]decane system[9] gave only unrearranged

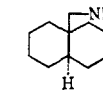
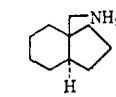
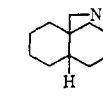
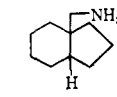
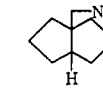
(7) W. G. Dauben and C. D. Poulter, *J. Org. Chem.*, **33**, 1237 (1968).
(8) P. R. Schleyer, P. R. Isele, and R. C. Bingham, *ibid.*, **33**, 1239 (1968).

Table II. Rearrangement Pathways for the Ester Solvolysis of the Bicyclo[*m.n.*0]alkane-1-methyl Series

Substrate	Ring expansion (%)	Bridging (%)	Rel rate,[h] 100°
	100	0	4.6
	91.1	8.9	
	100	0	4.3
	68.0	32.0	1.5×10^2
	4.0	96.0	1.0×10^3
	0	100	1.1×10^4
	0	100	5.3×10^4
	0	100	7×10^6

[a] J. B. Rogan, Dissertation, University of California, Berkeley, Calif., 1955. [b] T. L. Westman, Dissertation, University of California, Berkeley, Calif., 1960. [c] J. W. McFarland, Dissertation, University of California, Berkeley, Calif., 1957. [d] F. T. Bond, Dissertation, University of California, Berkeley, Calif., 1961. [e] See ref 5. [f] K. B. Wiberg, private communication. [g] See ref 2. [h] Relative to neopentyl *p*-toluenesulfonate.

Table III. Rearrangement Pathways for the Deamination of the Bicyclo[*m.n.*0]alkane-1-methyl Series

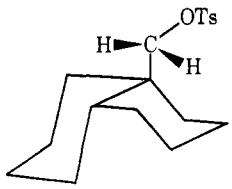
Substrate	Ring expansion (%)	Bridging (%)
	2.7	97.3
	19.7	80.3
	25	75
	36.3	62.2
	25.8	74.2

[a] See footnote *b* of Table II. [b] See footnote *c* of Table II. [c] See footnote *e* of Table II. [d] See ref 5.

products upon solvolysis or acid treatment. Therefore, the decalylcarbinyl and the hydrindanylcarbinyl compounds are not reacting *via* a pathway giving first the bridged product with subsequent rearrangement to give a more stable isomer.

Until this present study was completed, all the bicyclo[*m.n.*0]alkane-1-methyl compounds investigated had rearranged to give predominately the product resulting from the maximum release of ring strain. However, the bicyclo[4.2.0]octane-1-methyl system gives exclusively the bicyclo[4.2.1]nonane system releasing an estimated 13.6 kcal/mol of strain energy rather than giving the bicyclo[4.3.0]nonane system which would have released an estimated 19.9 kcal/mol of strain energy. Either the relative energy estimates are in error or migration of the zero-bridge bond becomes increasingly preferred for some other reason.

An indication that the latter suggestion is correct can be gained by examination of the results summarized in Table III for the deamination of the carbinylamines of this series. It is seen that in all the cases the migration of the zero bridge is highly preferred. It is generally agreed that in such a reaction the rearrangement has not progressed far along the reaction coordinate at the transition state. Similarly, in the solvolysis of highly strained systems it is to be expected that the leaving group will have moved much less before the rearrangement starts than in unstrained systems. Thus, the activated complex bears more and more relationship to the starting material and estimation of the steric interactions encountered in this complex can be achieved by consideration of the nonbonded atom interactions in the starting material. Examination of Dreiding models of the starting material clearly shows that minimum interactions develop when the carbinyl group is so arranged that the two carbon atoms of the ring juncture, the carbinyl carbon, and the oxygen atom of the ester are coplanar.[10] Such an arrangement places



the zero-bridge bond in the best orientation for participation with the p lobe developing as the ester group departs during ionization. Therefore, the increasing extent of the zero-bridge migration as the solvolysis rates become faster and also the large preference for the zero-bridge bond migration in the facile deaminations of all the systems can be accounted for by this increasing resemblance of the steric interactions in the activated complex to those in the starting material. It is to be appreciated that in the activated complex only a portion of the total ring strain release is felt and from the slope of the curve in Figure 1, it appears that about 20% or less is released in the complex. The maximum difference between any of the possible products (except in the bicyclo[2.2.0]hexane-1-methyl system) is about 6.3–6.5 kcal/mol. Hence, strain release energies which distinguish pathways at the activated complex stage may be in the range of 1.0–1.5 kcal/mol. Thus, it is evident that as nonbonded atom interactions play an increased role in the activated complex, sufficient energy differences can be envisioned to recognize their importance in controlling the reaction pathway.

With the compounds having the slower rates of solvolysis (*i.e.*, bicyclo[4.4,0]decane-1-methanol and bicyclo[4.3.0]nonane-1-methanol) the preferred ring expansion to another bicyclo[*m.n.*0]alkane system is dictated by the fact that the geometry of their activated complexes are not sufficiently controlled by nonbonded atom interactions to overcome the driving force favoring the more thermodynamically stable ring system. Although such a generalization permits one to predict the product of the solvolytic reaction, it is not clear from the result of the present study whether this stability factor predominates before or after the activated complex. In the present study where only the rates and products of the solvolysis reactions have been observed no definite answer to the question of anchimeric assistance is available for these slower reacting members of the series. Only by study of the structure of the ion, itself, will a more definitive answer be obtained.

In summary, the large rate enhancement for the faster bicyclic neopentyl compounds indicates that strain release is felt in the activated complex, demanding that ionization and rearrangement are concerted. In these cases, the favored migration of the zero bridge is due to the greater release of nonbonded atom interactions. For bicyclic neopentyl systems whose rates of solvolysis are similar to the neopentyl system, itself, the favored migration is that which results in maximum release of hydrocarbon ring strain. The extent of carbon bridging in the activated complexes of these latter compounds is uncertain.

Experimental Section

Melting points were determined with a Laboratory Devices Mel-Temp apparatus and are uncorrected. The nmr spectra were obtained from a Varian A-60 spectrometer with TMS as an internal standard. Infrared spectra were recorded with Perkin-Elmer 137 and 237 spectrometers. Consolidated 103 and Varian M-66 mass spectrometers provided the mass spectra. Vapor phase chromatography was performed on an Aerograph Model A-90-P (thermal conductivity detector) and Hi Fi Model 600-D (hydrogen flame detector). Analyses were performed by the microanalytical Laboratory, College of Chemistry, Berkeley, Calif.

Methyl Bicyclo[4,2.0]oct-3-ene-1-carboxylate (5). An ethereal solution of 1-cyclobutene-1-carboxylic acid was prepared, following the published procedure,[11] from 33 g (0.16 mol) of ethyl 1-bromocyclobutyl-1-carboxylate. This ethereal solution was added to 27 ml of butadiene in a metal pressure bomb cooled in a Dry Ice–acetone bath, and the sealed container maintained at 120° for 12 hr. The excess butadiene was allowed to evaporate at room temperature and the residue was esterified with a 200-ml ethereal solution containing 5 g of diazomethane. Distillation of the residue gave 5.87 g (0.035 mol; 22% yield from the bromoester) of isomeric C_9 methyl esters (bp 53–55° (2 mm)) which contained the equivalent of three sites of unsaturation. Analysis of this material by vpc on a 5 ft × 1/4 in., 5% Carbowax column at 125° showed three esters. The major component was 96% of the mixture and had a retention time just longer than the fastest moving component. The minor components were each present to the extent of 2%. The major component was the desired ester; ir (CCl_4) 2920, 1720, 1420, 1270, 1215, 1195, and 1095 cm^{-1}; nmr (CCl_4) δ 6.0–5.8 (m, 2), 3.6 (s, 3),

(9) P. R. Schleyer, K. B. Blanchard, and C. D. Wood, *J. Amer. Chem. Soc.*, **85**, 1358 (1963).

(10) A similar orientation of the atoms involved in the rearrangement of bicyclo[2.1.1]hexane-1-methyl systems has been postulated by K. B. Wiberg and B. A. Hess, Jr., *ibid.*, **88**, 4433 (1966).

(11) W. G. Dauben and J. Wiseman, *ibid.*, **89**, 3545 (1967).

3.1–2.7 (m, 1), 2.6–1.5 (m, 8); mass spectrum (70 eV) *m/e:* base peak, 137; molecular ion, 166.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.49; H, 8.73.

This Diels–Alder addition was also effected at 190° for 5 hr and a higher percentage of minor products was found. No addition occurred on standing at room temperature for 2 days.

Hydroboration and Jones oxidation of the minor esters indicated that the cyclobutyl ring was still intact and contained one of the double bonds since cyclobutanone derivatives were obtained; ir (CCl_4) 1780 cm^{-1} (C=O).

The minor component of shorter retention time was assigned structure **6**; ir (CCl_4) 2900, 1735, 1630, 1430, 1245, 1220, 1195, 1160, and 920 cm^{-1}; nmr (CCl_4) δ 6.1–5.5 (m, 3), 5.2–4.8 (m, 2), 3.6 (s, 3), 2.8–1.6 (m, 6); mass spectrum (70 eV) *m/e:* base peak, 107; molecular ion, 166.

Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found: C, 72.23; H, 8.64.

The minor component of longer retention time was assigned structure **7**; ir (CCl_4) 2900, 1705, 1635, 1425, 1270, 1240, 1205, 1080, and 915 cm^{-1}; nmr (CCl_4) δ 6.8 (broad s, 1), 6.0–5.5 (m, 1), 5.2–4.7 (m, 2), 3.6 (s, 3), 2.6–1.6 (m, 7); mass spectrum (70 eV) *m/e:* base peak, 107; molecular ion, 166.

Spinning-band distillation of the mixture of esters gave a 1.26-g fraction of pure methyl bicyclo[4.2.0]oct-3-ene-1-carboxylate (**5**). The other fractions were combined and chromatographed on neutral, activity II Alumina (5% diethyl ether–95% pentane as eluent) to remove the minor component **7** containing the conjugated ester. The other minor component **6** was not effectively separated from the major component; therefore, the mixture of **5** and **6** was redistilled on a spinning-band column to give 0.86 g of the desired ester **5**, giving a total of 2.11 g (8.1%) of isolated, pure **5** (no impurities were detected by vpc).

A 100-mg portion of methyl bicyclo[4.2.0]oct-3-ene-1-carboxylate (**5**) was saponified by refluxing for 3 hr in 1 ml of methanol containing 0.5 g of potassium hydroxide. Evaporative distillation gave a sample of analytically pure bicyclo[4.2.0]oct-3-ene-1-carboxylic acid; ir (CCl_4) 2910 (broad), 1680, 1425, 1400, 1290, 1255, and 1230 cm^{-1}; nmr (CCl_4) δ 13.5 (s, 1), 6.9 (broad s, 2), 3.2–2.7 (broad s, 1), 2.7–1.1 (m, 8).

Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95. Found: C, 71.18; H, 8.19.

Bicyclo[4.2.0]oct-3-ene-1-methanol (8). A stirred solution of 2.1 g (0.013 mol) of methyl bicyclo[4.2.0]oct-3-ene-1-carboxylate (**5**) in 150 ml of dry diethyl ether was cooled in an ice bath and 0.6 g (0.015 mol) of lithium aluminum hydride was added. The mixture was stirred at room temperature for 3 hr. Methanol and then saturated ammonium chloride solution were added until salts precipitated. The ether layer was decanted and the salts washed with ether. The combined ethereal solutions were washed with water, saturated sodium bicarbonate solution, water, and dried over anhydrous magnesium sulfate. The ether solution was filtered and the ether removed by rotary evaporation giving 1.6 g (92% yield) of bicyclo[4.2.0]oct-3-ene-1-methanol (**8**). Samples for spectral and analytical analysis were obtained by vpc (TCEP); ir (CCl_4) 3350, 3015, 2910, 1650, 1430, and 1025 cm^{-1}; nmr (CCl_4) δ 5.8 (s, 1), 4.2 (broad s, 1), 3.4 (s, 2), 2.7–1.1 (m, 9); mass spectrum (70 eV) *m/e:* base peak, 79; molecular ion, 138.

Anal. Calcd for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 78.10; H, 10.44.

This experiment was also done on 2.4 g of mixed esters giving a 96% yield of alcohols.

Bicyclo[4.2.0]octane-1-methanol (9). A mixture of 0.2 g of platinum oxide (84%) and 10 ml of 95% ethanol was shaken under a hydrogen atmosphere for 30 min. A 1.60-g (0.0116 mol) portion of bicyclo[4.2.0]oct-3-ene-1-methanol (**8**) in 25 ml of 95% ethanol was added to the hydrogenation vessel and the mixture was shaken under a hydrogen atmosphere for 2 hr. The platinum catalyst was filtered, the solution was concentrated by rotary evaporation, and the residue was taken up into 50 ml of diethyl ether. The ethereal solution was dried over anhydrous magnesium sulfate and filtered. The ether was removed by rotary evaporation to give 1.45 g (0.0104 mol) of bicyclo[4.2.0]octane-1-methanol (**9**) (89% yield). Samples for spectral and analytical analysis were obtained by vpc (TCEP); ir (CCl_4) 3350, 2920, 1480, 1070, 1045, 1020, and 958 cm^{-1}; nmr (CCl_4) δ 4.0 (broad s, 1), 3.3 (s, 2), 2.5–1.1 (m, 13); mass spectrum (70 eV) *m/e:* base peak, 43; molecular ion, 140.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.10; H, 11.47.

Bicyclo[4.2.0]octane-1-methyl *p*-Toluenesulfonate (10). A 500-mg (0.358 mmol) portion of bicyclo[4.2.0]octane-1-methanol (**9**) was dissolved in 30 ml of dry pyridine, the stirred mixture was cooled in an ice–methanol bath, and 735 mg (5% in excess) of *p*-toluenesulfonyl chloride was added. After the material had dissolved, the solution was stored under refrigeration (0–5°) for 4 days. This solution was poured into 30 ml of iced 5% aqueous hydrochloric acid and extracted with pentane. The combined extracts were washed with 25 ml of iced 5% aqueous hydrochloric acid, three 50-ml portions of saturated sodium bicarbonate solution, and 50 ml of water, and dried over anhydrous magnesium sulfate. The ether was removed by rotary evaporation giving an oil which contained no starting alcohol but it had to be subjected to the washings and isolation again in order to give ester of analytical purity. The final amount of analytically pure bicyclo[4.2.0]octane-1-methyl *p*-toluenesulfonate isolated was 684 mg (0.233 mmol, 65% yield); ir (CCl_4) 2910, 2840, 1600, 1450, 1355, 1180, 1170, 1095, and 950 cm^{-1}; nmr (CCl_4) δ 7.4 (d of d, 4, J = 25 and 8 Hz), 3.7 (s, 2), 2.35 (s, 3), 2.3–1.1 (m, 13); mass spectrum (70 eV) *m/e:* base peak, 91; no molecular ion.

Anal. Calcd for $C_{16}H_{22}O_3S$: C, 65.31; H, 7.48; S, 10.90. Found: C, 65.04; H, 7.41; S, 10.77.

Kinetics of the Solvolysis of Bicyclo[4.2.0]octane-1-methyl *p*-Toluenesulfonate. The rate was determined in buffered acetic acid solution using the aliquots technique. The buffered solution was prepared by placing 236 mg (2.88 mmol) of dry sodium acetate in a 250-ml volumetric flask and adding freshly distilled acetic acid (containing 0.6% acetic anhydride) to the mark. The titrant solution was reagent grade acetic acid which was 0.00375 *N* in perchloric acid. End points of titrations of remaining sodium acetate were determined by a potentiometric technique (Metrohm Herisau E 336A and E 436E automatic potentiometric titrator, using a differential setting). The electrode was soaked in reagent grade acetic acid for 30 min before beginning the titration. The infinity titer was taken after 8.5 half-lives. The rate was determined by a plot of $\ln (V_t - V_\infty/V_0 - V_\infty)$ against time with the aid of the LSKINI computer program.[12]

Determination of Rearrangement Products of Bicyclo[4.2.0]-octane-1-methyl *p*-Toluenesulfonate. A 378-mg (1.29 mmol) portion of bicyclo[4.2.0]octane-1-methyl *p*-toluenesulfonate (analytically pure) was heated at 61° for 6 hr in 65 ml of acetic acid (same acid as used for rate determinations) containing 121 mg (15% excess) of dry sodium acetate. The solution was 0.02 *M* in ester. The solution was then cooled, poured into 60 ml of water, and extracted with six 30-ml portions of pentane. The combined extracts were washed with a saturated solution of sodium bicarbonate, and water, and dried over anhydrous magnesium sulfate. Evaporation on a rotary evaporator gave 190 mg of rearranged esters (about 1.0 mmol; 80% recovery). The mixture gave, on vapor phase chromatography on a 5-ft 10% TCEP column, a single acetate, 1-bicyclo-[4.2.0]nonanyl acetate, of analytical purity; ir (CCl_4) 2920, 1735, 1455, 1370, 1250, 1220, 1080, and 1020 cm^{-1}; nmr (CCl_4) δ 2.5–2.15 (m, 1), 2.15–1.75 (m, 9), 1.75–1.15 (m, 8); mass spectrum (70 eV) *m/e:* base peak, 83; no molecular ion.

Anal. Calcd for $C_{11}H_{18}O_2$: C, 72.49; H, 9.95. Found: C, 72.49; H, 9.96.

A 130-mg portion (approximately 0.8 mmol) of acetate and *p*-toluenesulfonate esters (9.6% tosylate) from the solvolysis of bicyclo[4.2.0]octane-1-methyl *p*-toluenesulfonate was placed in a 100-ml pear-shaped, three-necked flask fitted with a Dry Ice condenser and a glass mechanical stirrer. About 50 ml of ammonia was collected under nitrogen in a 100-ml round-bottomed flask fitted with a Dry Ice condenser and 500 mg of lithium metal was added. The ammonia was then distilled into the three-necked reaction vessel *via* Tygon tubing containing a cotton plug (to filter any iron particles). About 2 ml of dry diethyl ether was added to enhance the solubility of the *p*-toluenesulfonate and then 600 mg (85 mmol) of chopped lithium wire was added. The blue color persisted for 20 min. A 5.1-g (160 mmol) portion of methanol was then added slowly. This destroyed the blue color. After 1 hr, 8.55 g (160 mmol) of ammonium chloride was added, the ammonia was evaporated, and approximately 50 ml of water was added. The solution was extracted with three 30-ml portions of diethyl ether, washed with saturated solutions of sodium bicarbonate and sodium chloride, and dried over anhydrous magnesium sulfate. After filtra-

(12) Professor A. Streitwieser, Jr., kindly provided copies of LSKINI and ACTENG computer programs, both of which were developed by Professor D. F. Detar, Florida State University.

tion and evaporation, 87 mg of residue remained which contained 53 mg (48% recovery) of alcohol, the remainder being diethyl ether. There was only one alcohol, 1-bicyclo[4.2.1]nonanol, by vpc on a 5-ft 10% TCEP column; mp 129.0–131.0° (sealed capillary; phase, changes at 66 and 81°); ir (CCl_4) 3350, 2900, 1455, 1345, 1080, 1050, 1025, and 975 cm^{-1}; nmr (CCl_4) δ 2.4–2.0 (m, 3), 2.0–1.0 (m, 3); mass spectrum (70 eV) *m/e:* base peak, 83; molecular ion, 140.

High-resolution mass spectrum (from reduction of analytically pure acetate) calcd for $C_9H_{16}O$: 140.1201. Found: 140.1206.

A separate solvolysis mixture of rearranged acetate and *p*-toluenesulfonate esters was reduced with lithium aluminum hydride using the same procedure as outlined for the preparation of bicyclo-[4.2.0]oct-3-ene-1-methanol. A single alcohol was formed whose spectral properties were identical with those of 1-bicyclo[4.2.1]-nonanol.

To a 94-mg portion (0.67 mmol) of 1-bicyclo[4.2.1]nonanol (vpc pure) in 3 ml of dry pyridine (distilled from KOH and BaO and stored over BaO) was added with stirring 350 μl (3.8 mmol) of phosphorus oxychloride. The Teflon stir bar turned black during the reaction. After 3 hr at room temperature the solution was clear. It was then maintained at 50–60° for 40 hr under a nitrogen atmosphere. The solution was reddish brown after 24 hr. The solution was then cooled to room temperature, poured into 30 ml of ice water, and extracted with three 25-ml portions of diethyl ether. The combined ether extracts were washed with two 25-ml portions of 10% aqueous hydrochloric acid and with saturated solutions of sodium bicarbonate and sodium chloride. The ethereal solution was then dried over anhydrous magnesium sulfate, filtered, and evaporated on a rotary evaporator. About 50 μl of colorless liquid remained after evaporation. Analysis by vpc on a 5-ft 10% TCEP column at 140° showed two compounds were formed in a 5:1 ratio. The minor component of shorter retention time was not identified. The major component was 1-bicyclo[4.2.1]nonylchloride as was shown by ir, mass spectrum, and Beilstein test; ir (CCl_4) 2900, 1460, 1215, 985, 948, 925, and 840 cm^{-1}; mass spectrum (70 eV) *m/e:* base peak, 123; molecular ions, pair at 158 and 160 with relative heights 3.7:1.0.

Stability of Bicyclo[4.2.1]nonyl *p*-Toluenesulfonate (12d) to Solvolytic Conditions. Two acetic acid solutions of bicyclo[4.2.0]-octane-1-methyl *p*-toluenesulfonate (**10**) were prepared as before (for the titrimetric rate determination of **10**). Each solution was placed in a constant temperature bath (61.3°) for 6 hr (just over 10 half-lives of the bicyclo[4.2.0]octane-1-methyl *p*-toluenesulfonate rearrangement). Each of the two solutions then contained 10% bicyclo[4.2.1]nonyl *p*-toluenesulfonate (**12d**) and 90% bicyclo-[4.2.1]nonyl acetate (**12c**). In order to ascertain the solvolytic reactivity of **12d** under these conditions, three aliquots were removed from each of the solutions over the next 6.5 hr and titrated. An aliquot of the buffered acetic acid solvent was titrated to determine the theoretical infinity point. All the points for each of the solutions were essentially the same. The slight fluctuations which were observed show no trend and indicated that less than 4% of **12d** had reacted during 10 half-lives of the rearrangement of **10**.

1-Bicyclo[4,4,1]undecanol. A 3-g portion of *cis*-bicyclo[4.4.0]-decane-1-methylamine[13] was dissolved in 115 ml of glacial acetic acid at room temperature. A 4.15-g portion of sodium nitrite was added over 30 min. The mixture was stirred overnight at room temperature. A 250-ml portion of water was then added and the organic material was extracted with three 100-ml portions of pentane. The pentane extracts were combined and washed with saturated solutions of sodium bicarbonate and sodium chloride. The pentane layer was dried over anhydrous magnesium sulfate and the pentane removed by rotary evaporation.

The acetate which was formed was then dissolved in about 100 ml of dry diethyl ester and cooled with stirring in an ice bath. A 750-mg portion (100% excess) of lithium aluminum hydride was then added and the mixture was stirred for 2 hr. A saturated solution of ammonium chloride was added to precipitate the salts and the ether layer was decanted from the residue. This ether layer was then washed with a saturated solution of sodium bicarbonate and with water. The ethereal solution was dried over anhydrous magnesium sulfate and the ether was removed by rotary evaporation. The crude material was about 75% alcohol and 25% olefin. The desired alcohol was collected from an SE-30 preparative column at 150°.

Bicyclo[4.4.1]undecyl 1-Mesylate. A 170-mg portion (1 mmol) of 1-bicyclo[4.4.1]undecanol and 120 mg of methanesulfonyl chloride (5% excess) in 2 ml of benzene was stirred for 10 min in an ice bath. A 116-mg portion of triethylamine was added. The mixture was removed from the ice bath and allowed to stir an additional 10 min at room temperature. The salts were filtered and washed with benzene. The benzene was removed by rotary evaporation to give 470 mg of material; half of which was the desired ester, the other half was elimination product; ir (CCl_4) 2890, 1455, 1370, 1325, 1175, and 1145 cm^{-1}.

Bicyclo[4.4.1]undec-1-ene. About 100 mg of a mixture of 1-bicyclo[4.4.1]undecanol and bicyclo[4.4.1]undec-1-ene was treated with phosphorus oxychloride using a procedure analogous to that utilized to dehydrate 1-bicyclo[4.2.1]nonanol (**12b**). The product collected was purified by vpc; the material was identical with an authentic product.[13]

Acetolysis of Bicyclo[4,4,1]undecyl 1-Mesylate. A 170-mg mixture of bicyclo[4.4.1]undecyl 1-mesylate and bicyclo[4.4.1]-undec-1-ene was added to 6 ml of acetic acid and 75 mg of sodium acetate (100% excess) and refluxed for 23 hr (protected from moisture by a calcium chloride drying tube atop the reflux condenser). The solution was clear for the first 2 hr; after 14 hr the solution was dark brown. The solution was cooled, poured into 2.5 ml of water, and extracted with pentane. The pentane extracts were washed with saturated solution of sodium bicarbonate and sodium chloride and dried over anhydrous magnesium sulfate. The pentane was removed by rotary evaporation. Vpc and ir showed that greater than 90% of the product from the mesylate acetolysis was bicyclo[4.4.1]undec-1-ene.

Treatment of Bicyclo[4,4,1]undecyl 1-Mesylate with Lithium Perchlorate and Acetone. A mixture of bicyclo[4.4.1]undecyl 1-mesylate and bicyclo[4.4.1]undec-1-ene was added to an ampoule and 6 ml of reagent grade acetone and 2 equiv (115 mg) of lithium perchlorate were added. The tube was evacuated to about 3 mm as the tube was cooled to Dry Ice–acetone temperature and was sealed. This ampoule was then maintained at 117° for 2 days (approximately 48 hr). The solution was deep red. The ampoule was opened and its contents emptied into 15 ml of water. This mixture was extracted with three portions of pentane. The pentane extracts were washed with a saturated solution of sodium bicarbonate, and water, and dried over anhydrous magnesium sulfate. After filtration and rotary evaporation, the remaining liquid was subjected to vapor phase chromatography. Nine compounds were detected by vpc on a 10 ft × 1/4 in., 10% Carbowax (10% KOH) column, but none were alchol or olefin derivatives of either the 1-bicyclo[4.4.1]undecane system or the 1-bicyclo[5.3.0]undecane system.

Attempted Acid Equilibration of Bicyclo[4,4,1]undec-1-ene. About 100 mg of bicyclo[4.4.1]undec-1-ene was placed in an nmr tube and 50 μl of concentrated sulfuric acid and 50 μl of acetic acid were added. The tube was sealed and maintained at 117° for 4 days. The triplet for the starting material between δ 5.0 and 5.5 disappeared and was replaced by a low-field absorption at δ 6.5–7.0. The solution turned black in less than 1 hr and was sludgy at the end of the reaction time. The contents of the tube were emptied into 2 ml of water and extracted with six portions of pentane. The pentane extracts were washed with three portions of a saturated sodium bicarbonate solution, dried, and concentrated by rotary evaporation. The ir showed no acetates: the mass spectrum showed the molecular ion to be 146, not the 150 of the starting material (loss of 4 hydrogens). The uv spectrum of this material in hexane showed a maximum at 215 mμ with a shoulder at 255 mμ (the intensity was not accurately determined but ϵ seemed to be >10,000). Vpc analysis on a 5-ft 10% TCEP column at 105° showed two peaks (1.5:1). It appears that the system aromatized.

This same general procedure was repeated using *p*-toluenesulfonic acid (monohydrate) and an equivalent amount of acetic anhydride in place of the sulfuric acid. The solution was maintained at 117° for 4 days. Three unidentified products were detected by vpc. None of these products was starting olefin or bicyclo[5.4.0]undec-1-ene.

Attempted Acid Equilibration of Bicyclo[5.4.0]undec-1-ene. About 100 mg of bicyclo[5.4.0]undec-1-ene containing about 10% of isomeric olefins was placed in an nmr tube. About 50 μl of concentrated sulfuric acid and 400 μl of acetic acid were added and the tube was sealed. An nmr was run. The tube was maintained at 117° for 48 hr. An nmr was run after 2 hr, 24 hr, and 48 hr. No change was observable (no vinyl protons appeared). The contents of the tube were deep red in 2 hr and black shortly thereafter. The tube was worked up as with the equilibration attempts above and the residue (approximately 150 mg) was vpc collected. The major component (approximately 85%) was bicyclo[5.4.0]undec-1-ene, indicating its stability to these conditions.

(13) (a) See footnote *b* of Table II; (b) T. L. Westman and R. D. Stevens, *Chem. Commun.*, 459 (1965).