difficulties. The energies of eclipsed and staggered ethanes were calculated giving a difference of 0.0034. Using the conversion factor obtained herein, this is 0.7 kcal/mole whereas the observed value is 3 kcal/mole. Thus, for cycloalkanes and similar molecules, the energy due to the torsional barrier must be added to the calculated energy. Further, in connection with the data in Table V, the energy of the ethylene ion-radical was calculated. Unlike all the other cases, two minima were found. The first had r (CH) = 1.139, r (CC) = 1.300, A (CCH) = 138.0 and ΔE (atom.) = 2.4114. The second had r (CH) = 1.127, r (CC) = 1.450, A (CCH) = 121.7 and ΔE (atom.) = 2.4293. Using these energies, one calculates a ΔH (atom.) which is 1 ev too low. It is possible that the two conformations and the error in calculated energy are related, and that, for example, the ethylene radical cation is nonplanar. The vinyl radical and cation were not considered since the energies of these species appear not to be well established.

Experimental Section

The energies were calculated using the program written by G. A. Segal which was made available through the Quantum Chemistry Program Exchange at Indiana University. Initially, the program was modified so that the carbon and hydrogen β-proportionality constants and average ionization potentials were chosen within a predetermined range (about ±20% of the original value) using a random number generator. For each set of parameters, the energies of three ethane and three ethylene structures differing in C–C bond length, were calculated and the equilibrium geometry was obtained assuming a parabolic function. The data thus obtained are shown in Figure 1.

The data shown in Table II were obtained by calculating the energies of a number of structures for each molecule. For methane, three C–H bond lengths were used, and a parabolic function was assumed. For ethane and ethylene, three C–H bond lengths, three C–C bond lengths, and three C–C–H bond angles were taken. This set leads to 27 structures. Initially, the energies of each of the structures was obtained and the energies were fitted to a general quadratic function of the three geometrical parameters. A very good fit was obtained. From this, the equilibrium geometry and energy were easily obtained. The fitting procedure was repeated using only the odd-numbered structures, giving a set of 14. No significant difference in result was noted, and subsequent calculations were based on a set of 14 structures.

The data in Table III were obtained in a similar fashion, using the parameters on the last line of Table II. In the case of propane, the methyl group geometry found in ethane was assumed, and only the geometry about the central carbon was varied. The C–H bond length was taken as 1.12 A. The energies shown in Table IV were obtained using β_H = 10.0, β_C = 17.5, I (1s) = 7.176, I (2s) = 10.3, and I (2p) = 6.3. The CH bond lengths were taken as 1.12 A except for acetylene for which 1.10 A was used. The C–C lengths were rounded to the nearest 0.01 A, and the calculated bond angles were used. Butane was assumed to have the geometrical parameters calculated for propane. The heat of formation of carbon was taken as 170.39 kcal/mole and that for hydrogen was 51.62 kcal/mole.

The results summarized in Table V were obtained in the same fashion as that of Table III. The heats of atomization were calculated for the process leading to a neutral carbon atom, hydrogen atom, and, in the case of the cations, a proton. The heat of formation of the latter was taken as 365.14 kcal/mole. The zero-point energies of the radical cations were assumed to be the same as that for the hydrocarbons. The difference in zero point energy between a hydrocarbon and its radical cation might be expected to be roughly constant, leading to relatively little error in the calculated slope. The radicals were assumed to have a zero-point energy equal to that of the parent hydrocarbon less one C–H stretching vibration (3000 cm^{-1}) and two bending vibrations (1000 cm^{-1}). The cations were assumed to have the same zero-point energy as the radicals.

Solvolysis of Bicyclo[2.1.0]pentane-5-methyl and Bicyclo[3.1.0]hexane-6-methyl Tosylates[1]

Kenneth B. Wiberg and Arthur J. Ashe, III[2]

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut. *Received June 21, 1967*

Abstract: The rates and products of the solvolysis of the *exo*- and *endo*-bicyclo[2.1.0]pentane-5-methyl and bicyclo[3.1.0]hexane-6-methyl tosylates in acetic acid and in aqueous ethanol are reported. The data suggest that ionization leads first to the cyclopropylcarbinyl cation. The nature of reactions leading from these ions to the products is discussed.

Cyclopropylcarbinyl and cyclobutyl derivatives are of considerable interest because of their high solvolytic reactivity.[3] A number of suggestions have been made concerning the structure(s) of the ions.[3,4] Recently, the tertiary cyclopropylcarbinyl cations have been shown *via* nmr spectroscopy to have an unrearranged structure.[5] We have examined the solvolysis of the bicyclo[3.1.0]hexane-6-methyl tosylates[6] and the bicylo[2.1.0]pentane-5-methyl tosylates[7] and have concluded that the ion initially formed from these primary alcohol derivatives also must have the cyclopropylcarbinyl cation structure. The same conclusion has been reached by Schleyer and Van Dine[8] in their examination

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[1] This work was supported by a grant from the National Institutes of Health and forms part of the Ph.D. thesis of A. J. A., 1967.

[2] National Science Foundation Predoctoral Fellow, 1963–1966.

[3] *Cf.*, J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509, 3542 (1951); R. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver, and J. D. Roberts, *ibid.*, **81**, 4390 (1959).

[4] S. Winstein and E. Kosower, *ibid.*, **81**, 4399 (1959).

[5] C. U. Pittman, Jr., and G. A. Olah, *ibid.*, **87**, 2998 (1965); N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln, and R. E. Fruit, Jr., *ibid.*, **87**, 3000 (1965).

[6] K. B. Wiberg and A. J. Ashe, III, *Tetrahedron Letters*, 1553 (1965).

[7] K. B. Wiberg and A. J. Ashe, III, *ibid.*, 4245 (1965).

[8] P. von R. Schleyer and G. W. Van Dine, *J. Am. Chem. Soc.*, **88**, 2321 (1966).

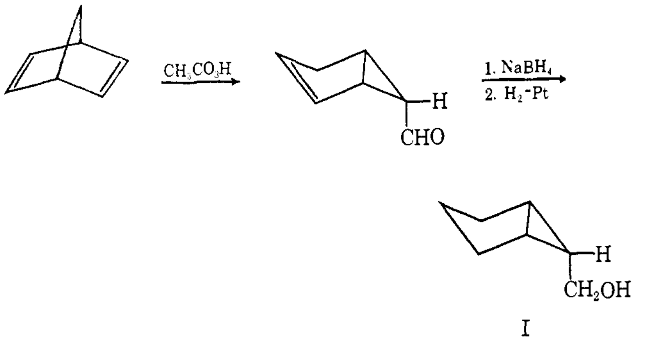
Table I. Acetolysis of Bicyclo[3.1.0]hexane-6-methyl Tosylates

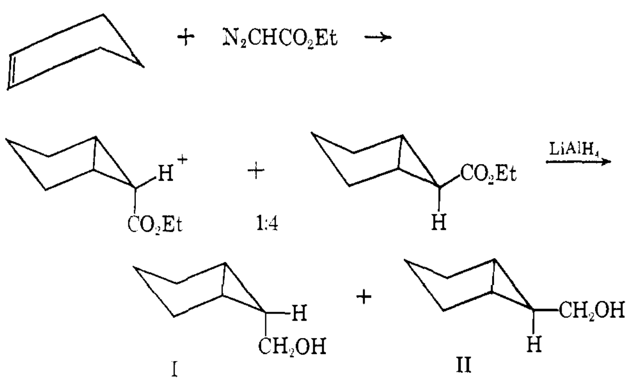
Tosylate	Temp, °C	Internal return, %	$k \times 10^3$,[a] sec^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
exo-Bicyclo[3.1.0]hexane-6-methyl (II)	17.0	50	5.35 ± 0.15	18.8	−4
	27.0		16.4 ± 0.1		
endo-Bicyclo[3.1.0]hexane-6-methyl (I)	17.0	26	4.53 ± 0.01	18.4	−6
	27.0		13.5 ± 0.5		
Cyclopropylcarbinyl[b]	17.0	33	0.10	21.8	−2

[a] The rate constants are the average of two determinations; the deviation given is one-half the difference between the two rate constants. [b] D. D. Roberts, *J. Org. Chem.*, **29**, 294 (1964), reported for the acetolysis $\Delta H^{\ddagger} = 16.7$ kcal/mole and $\Delta S^{\ddagger} = -19$ eu. However, his rates referred only to the formation of acetate and were estimated from initial slopes. Mr. J. Longanbach has determined the total rates of ionization (acetate formation plus internal return) at 17.2° ($k = 1.05 \times 10^{-4}$ sec^{-1}) and at 40.0° (1.78×10^{-3} sec^{-1}), giving the activation parameters listed in the table. Roberts' rate constants for ethanolysis are probably correct since no internal return was found.

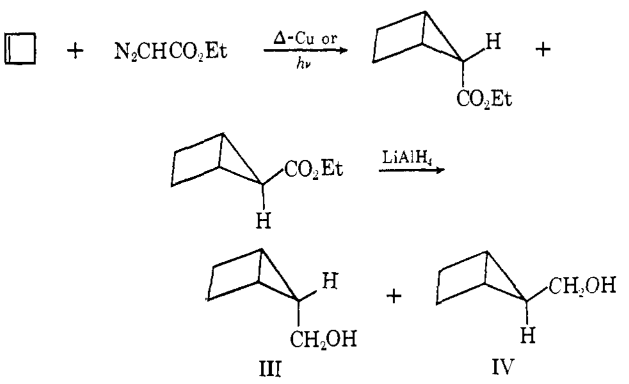
of the 2- and 3-methylated cyclopropylcarbinyl derivatives. We now wish to record in detail our observations concerning the bridged cyclopropylcarbinyl derivatives.

endo-Bicyclo[3.1.0]hexane-6-methanol was prepared by the hydrogenation and sodium borohydride reduction of *endo*-bicyclo[3.1.0]hex-2-ene-6-carboxaldehyde which Meinwald, Labana, and Chada[9] obtained by the reaction of norbornadiene with peracetic acid. A mixture of the *exo* and *endo* isomers was obtained by the reaction of cyclopentene with ethyl diazoacetate followed by lithium aluminum hydride reduction. The alcohols, formed in a 4:1 *exo*:*endo* ratio, could easily be separated by preparative vpc.





A mixture of *exo*- and *endo*-bicyclo[2.1.0]pentane-5-methanols was obtained by heating a mixture of cyclobutene and ethyl diazoacetate to 80° in the presence of copper powder, followed by lithium aluminum hydride reduction. The alcohols were obtained in an 85:15 ratio. Since it is known that the copper-catalyzed addition of diazoacetate ester to double bonds has a strong preference for exocyclic addition,[10] the predominant isomer presumably has the *exo* configuration. In order to obtain reasonable quantities of the *endo* isomer, the photochemical reaction, which usually gives a less selective addition,[11] was examined. Here, a 1.4:1 ratio was obtained along with a considerable amount of C–H insertion product.



The four alcohols, I–IV, could be converted to their tosylates by reaction with *p*-toluenesulfonyl chloride and powdered potassium hydroxide in ether at 0°. After recrystallization, they could be stored at −80° until used. However, a few minutes at room temperature was sufficient to destroy them.

Bicyclo[3.1.0]hexane-6-methyl Tosylates

The rates of acetolysis of the tosylates derived from I and II were determined using the procedure given in the Experimental Section. The rate constants are summarized in Table I. In each case, internal return product was found, and the rate constants measured by observing the appearance of *p*-toluenesulfonic acid correspond to the sum of the constants for solvolysis and internal return and therefore refer to the apparent rate of ionization. The activation parameters are based on only a 10° temperature range because acetic acid cannot be cooled significantly below 17°, and the rate becomes too large to measure above 27°.

The amount of internal return was determined by heating the reaction solution at length in order to liberate the theoretical amount of *p*-toluenesulfonic acid. In the case of the *endo*-tosylate, there were two internal return products. The first reacted an order of magnitude slower than the starting tosylate while the second liberated *p*-toluenesulfonic acid only after heating at higher temperatures. *In situ* determination of the rate of solvolysis of the reactive internal return product gave a rate constant of 1×10^{-4} sec^{-1} at 17°.

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(9) J. Meinwald, S. S. Labana, and M. S. Chada, *J. Am. Chem. Soc.*, **85**, 582 (1963).

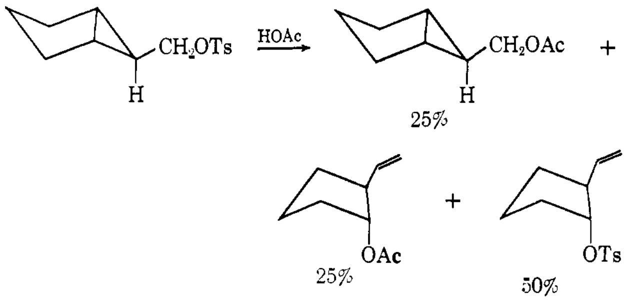
(10) W. von E. Doering and T. Mole, *Tetrahedron*, **10**, 65 (1960).

(11) The thermal reaction with cyclohexene gives a 17:1 *exo*:*endo* ratio, whereas the photochemical reaction gives a 1.6:1 ratio: P. S. Skell and R. M. Etter, *Proc. Chem. Soc.*, 443 (1961).

Since both tosylates (I and II) react with similar rates, the difference in geometry had no significant effect on the free energy of activation. Further $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are essentially the same for the two isomers. The *exo*- and *endo*-tosylate react 82 and 44 times as fast as cyclopropylcarbinyl tosylate. This is the normal effect of 2,3-dialkyl substitution.[8] *trans*- and *cis*-2,3-dimethylcyclopropylcarbinyl 3,5-dinitrobenzoates react 124 and 82 times as fast as the unsubstituted compound in 60% aqueous acetone.

The product studies were carried out in the usual fashion. The acetates were separated from internal return products by distillation, and the acetates were separated by vpc and identified by a comparison of their spectra with those of authentic samples.

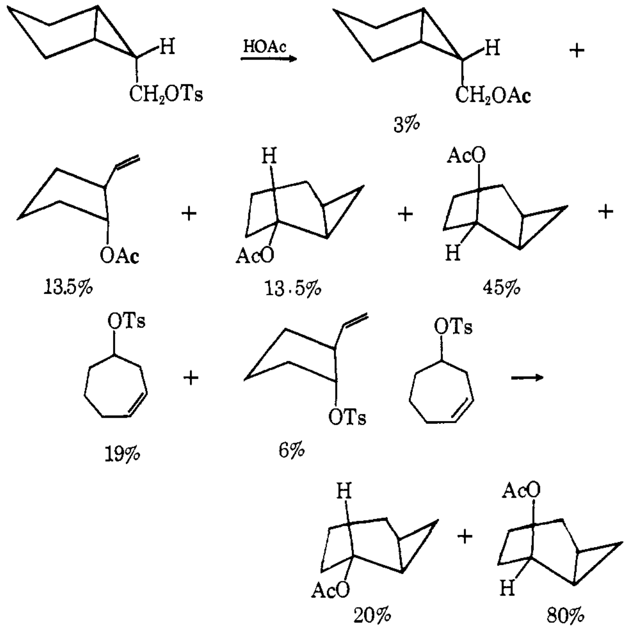
The *exo*-tosylate gave two acetates in equal amount. One was the parent acetate and the other was shown to contain a vinyl group by its nmr spectrum. This suggested it might be the homoallylic product, 2-vinylcyclopentyl acetate. The latter was prepared by the reaction of vinyl lithium with cyclopentene oxide followed by acetylation, and presumably was the *trans* isomer. The synthetic acetate was identical with that formed in the solvolysis. The internal return product was identified as *trans*-2-vinylcyclopentyl tosylate.



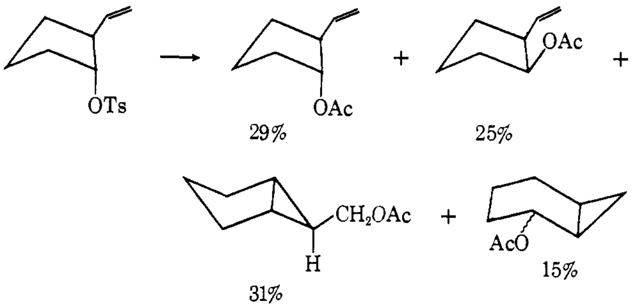
endo-Bicyclo[3.1.0]hexane-6-methyl tosylate gave a more complex mixture. The acetate products were not readily separated by vpc and were reduced to the more easily separated alcohols. Four alcohols were found in the ratio of 18:10:18:4 in order of retention time on a Carbowax column. The first was *trans*-2-vinylcyclopentanol while the fourth was the parent alcohol. The second and third appeared to be cyclopropane derivatives because of their high-field nmr signal. They were shown to be identical with the two epimeric 2-norcaranols which were prepared by Cope, *et al.*,[12] *via* the solvolysis of 3-cyclohepten-1-yl brosylate.

The cycloheptenyl tosylate underwent solvolysis in acetic acid with rate constants of 9.25 ± 0.05 × 10^{-5} sec^{-1} at 17.0° and 6.05 ± 0.15 × 10^{-4} sec^{-1} at 32.0°. These rate constants suggest that the tosylate may be the reactive internal return product obtained from the *endo*-tosylate. The products of the solvolysis were the two 2-norcaranyl acetates in a 4:1 *endo*:*exo* ratio.[12] This was identical with the ratio obtained from the solvolysis of the *endo*-tosylate.

When the acetolysis mixture from the *endo*-tosylate was worked up after about five half-lives, a mixture of two internal return products was isolated. Cleavage with sodium in liquid ammonia gave *trans*-2-vinylcyclopentanol and 3-cycloheptenol.



The common internal return product from both bicyclo[3.1.0]hexane-6-methyl tosylates, *trans*-2-vinylcyclopentyl tosylate, has also been subjected to acetolysis. The rate constants were 1.21 ± 0.01 × 10^{-4} sec^{-1} at 69.8° and 5.98 ± 0.06 × 10^{-4} sec^{-1} at 85.0°. Analysis by vpc showed four acetates in a ratio of 29:25:31:15. The first and third were found to be *trans*-2-vinylcyclopentyl acetate and *exo*-bicyclo[3.1.0]hexane-6-methyl acetate. The fourth was shown to be a mixture of the 2-norcaranyl acetates in a 4:1 ratio. The first acetate was not examined in detail, although the similarity of its nmr spectrum with that of *trans*-2-vinylcyclopentyl acetate made it appear likely that it was the *cis* isomer.



Valuable information about solvolytic reactions often may be obtained by a comparison of rates[13] and products in different solvents. Data for aqueous alcohol solutions are summarized in Table II. Besides the rate constants, the table gives the *m* and **N** values derived from[13]

$$\log (k/k_0) = m\mathbf{Y}$$

and

$$d \ln k = (d \ln k/d\mathbf{Y})_{\mathbf{N}} d\mathbf{Y} + (d \ln k/d\mathbf{N})_{\mathbf{Y}} d\mathbf{N}$$

The relatively large values of *m*, indicating a high sensitivity to solvent ionizing power, and the low values of **N**, indicating a low sensitivity to solvent nucleophilicity, indicate that these are limiting solvolyses and that the

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[12] A. C. Cope, C. H. Park, and P. Scheiner, *J. Am. Chem. Soc.*, 84, 4862 (1962).

[13] E. Grunwald and S. Winstein, *ibid.*, 70, 846 (1948); S. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, 73, 2700 (1951).

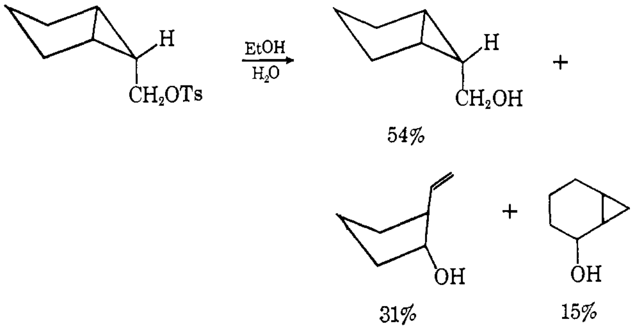
Table II. Ethanolysis of the Bicyclo[3.1.0]hexane-6-methyl Tosylates

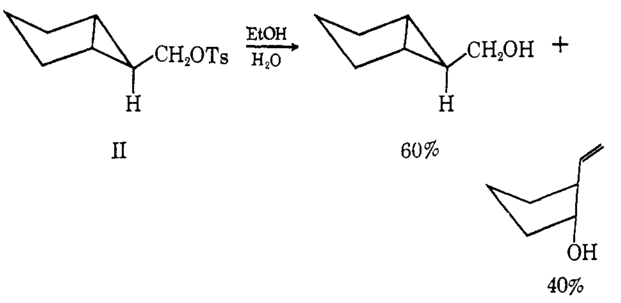
Tosylate	Temp, °C	% EtOH	Y^a	Internal return, %	$k \times 10^4$, sec^{-1}	m	N
Cyclopropylcarbinyl[b]	20	80	0.0	0	11.3	0.75	1.07
	20	100	−1.974		0.32		
	0	80	0.0		0.54[c]		
exo	0	95	−1.287	36	7.6	0.82	0.44
		80	0.0		88.0		
endo	0	95	−1.287	9	5.3	0.79	0.47
		80	0.0		56.0		

[a] A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2770 (1956). [b] See footnote *b*, Table I. [c] Extrapolated from higher temperatures for 100% ethanol, then corrected to 80% using m = 0.75.

bridged compounds behave in the same way as cyclopropylcarbinyl itself.

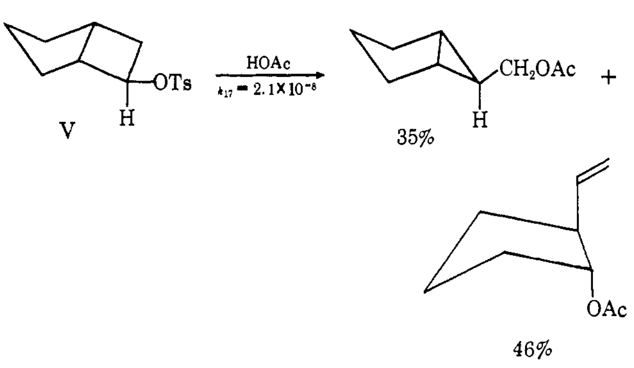
Since ethanol is a more nucleophilic solvent than acetic acid, one would expect carbonium ion lifetimes to be shorter in the former than in the latter. Thus, if a solvolytic reaction involves a series of rearrangements, one should intercept the process at an earlier stage using aqueous alcohol rather than acetic acid. The alcohol products obtained in 80% alcohol are shown below. Presumably the ether products are analogous.

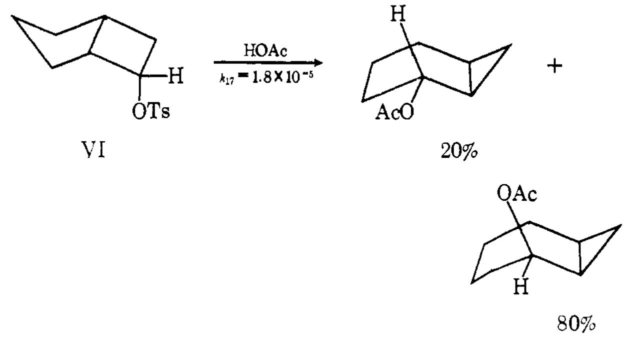




The *exo* isomer gave about the same proportion of products as found in the acetolysis. However, with the *endo* isomer, the parent alcohol and *trans*-2-vinylcyclopentanol have increased markedly at the expense of the 2-norcaranols.

Because of the apparent relationship between cyclopropylcarbinyl and cyclobutyl derivatives, and the possiblity that solvolytic reactions of the two may have a common intermediate, it is of interest to compare the above results with those for the isomeric bicyclo[3.2.0]heptan-6-ols studied by Goering and Nelson.[14] Their results were

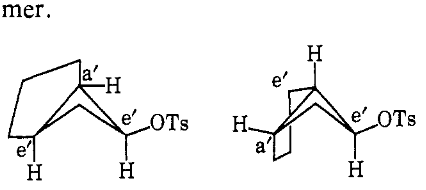




The products from the *exo* isomer are the same and in essentially the same proportion as we found with *exo*-bicyclo[3.1.0]hexane-6-methyl tosylate, except for the internal return product, *trans*-2-vinylcyclopentyl tosylate. However, the latter is more reactive than V and therefore would not be found even if formed. It seems reasonable to assume a common intermediate in the solvolyses of V and of II-tosylate.

The products from VI and I-tosylate were, however, different and the difference is enhanced in aqueous ethanol. Thus, in this case different intermediates must be involved at least initially. What factors may account for the difference in behavior between the two pairs of isomers?

Cyclobutane is nonplanar and is puckered by about 35°,[15] leading to pseudo-axial and pseudo-equatorial positions. When a cyclopentane ring is *cis*-fused to the cyclobutane ring, one of the bonds must be in a pseudo-axial position and the other in a pseudo-equatorial position. This will permit the tosyloxy group to assume the preferrred pseudo-equatorial position in either isomer.



endo *exo*

Further, in an examination of 1,3-bridged cyclobutanes[16] we have found that an equatorial tosyloxy group is necessary in order to have cyclobutyl participation. Thus, the conformations given above are those required for such participation.

If we consider the *endo* isomer, it can be seen that two modes of C–C bond participation are possible.

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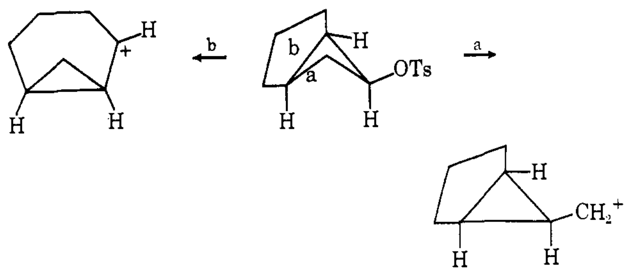
(14) F. F. Nelson, Ph.D. Thesis, University of Wisconsin, 1960.

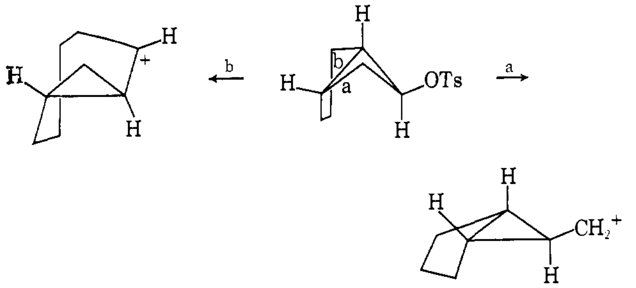
(15) A. Almennigen, O. Bastiansen, and P. N. Skanke, *Acta Chem. Scand.*, **15**, 711 (1961); P. N. Skanke, Ph.D. Thesis, University of Oslo, 1960.

(16) K. B. Wiberg and R. Fenoglio, *Tetrahedron Letters*, 1273 (1963); K. B. Wiberg and B. A. Hess, Jr., *J. Am. Chem. Soc.*, **89**, 3015 (1967).



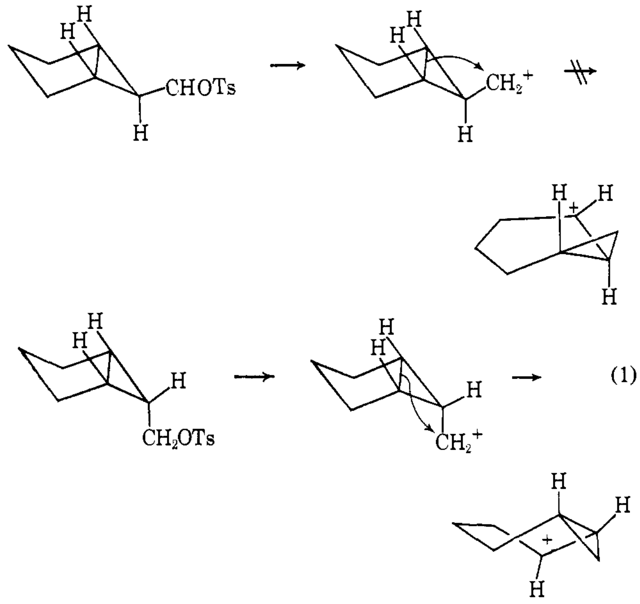
The migration of the a bond during ionization of the tosylate would lead to the *endo*-bicyclo[3.1.0]hexane-6-carbinyl system, whereas migration of the b bond would lead to the 2-norcaranyl ion. Since b participation will lead to the more highly alkylated cation, it would be expected to predominate. In accordance with this expectation the 2-norcaranyl acetates were the exclusive products of acetolysis.

The same two possibilities are open for the *exo* isomer.



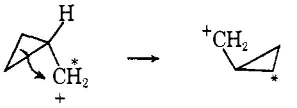
Path a again leads to a bicyclo[3.1.0]hexane-6-carbinyl cation, now with the *exo* geometry. However, path b would give the 2-norcaranyl ion with a *trans*-fused cyclopropane ring. This would be expected to be a high-energy path and would not be expected to occur. Thus, in this case, path a is followed. The difference in reactivity between the two isomers may be accommodated in the same way. The reaction of the *endo* isomer leads to a more stable secondary cation and might be expected to be more reactive than the *exo* isomer.

With the bicyclo[3.1.0]hexane-6-methyl derivatives, it seems fairly clear that the reaction leads at first to the corresponding cyclopropylcarbinyl cations. With the *endo* isomer, there is a further rearrangement to the 2-norcaranyl system, while the *exo* isomer has undergone no such rearrangement. Formally, a process which could produce the 2-norcaranyl ion would involve an attack of $-CH_2^+$ on the C_2–C_5 cyclopropyl bonds. In the case of the *exo* isomer, such a process would again produce the *trans*-fused 2-norcaranyl system. As a result, it does not occur (see eq 1).

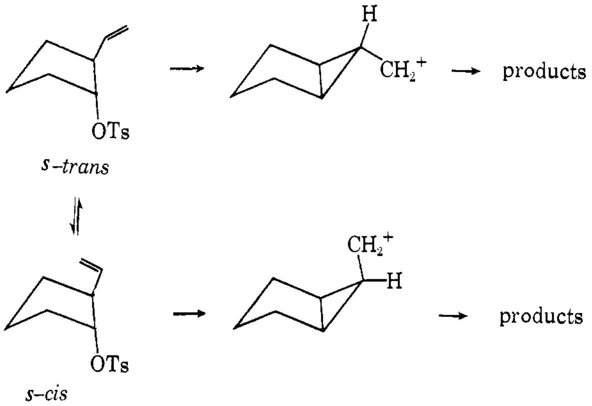


(1)

Although this explanation for the differences among the compounds may be an oversimplification, it seems almost certain that it contains the most essential parts of any explanation. It might be noted that the effect of ethanol–water on the product composition, leading to larger quantities of the parent alcohol starting with the *endo* isomer, is in accord with the above picture. Further, the C^{14} scrambling observed by Roberts, *et al.*, in the deamination of cyclopropylcarbinylamine may result from a process such as that given above rather than involving equilibrating bicyclobutonium ions.



Apart from *trans*-2-vinylcyclopentyl acetate and tosylate, no common products were found in the acetolyses of *exo*- and *endo*-bicyclo[3.1.0]hexane-6-methyl tosylates. On the other hand, *trans*-2-vinylcyclopentyl tosylate gives products which are derived from both *exo* and *endo* families. Clearly, the *exo*-bicyclo[3.1.0]hexane-6-methyl acetate is an *exo*-type product, while the 2-norcaranyl acetates are *endo*-type products. Since no interconversion was noted between the *exo* and *endo* families of ions, *trans*-2-vinylcyclopentyl tosylate must give both *endo*- and *exo*-type ions. The bicyclo[3.1.0]hexane-6-methyl cations are produced by interaction of the double bond of *trans*-2-vinylcyclopentyl tosylate with the generated positive charge at C_1. If the double bond is in the *s-trans* conformation, the product cation will be *exo*, whereas if the double bond has the *s-cis* conformation, the *endo* ion will be produced.



The *trans*-2-vinylcyclopentyl tosylate and acetate derived from *endo*-bicyclo[3.1.0]hexane-6-methyl tosylate probably does not come from a "classical" 2-vinylcyclopentyl ion. If such an ion were formed, initially it would be in a position to reclose to the *endo*-bicyclo-[3.1.0]hexane-6-carbonium ion. However, rotation of 180°, which might have an activation energy of only about 2 kcal/mole,[17] would produce an ion which

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(17) The barrier to rotation in propylene is 1.98 kcal/mole: D. R. Linde, Jr., and D. E. Mann, *J. Chem. Phys.*, 27, 868 (1957).

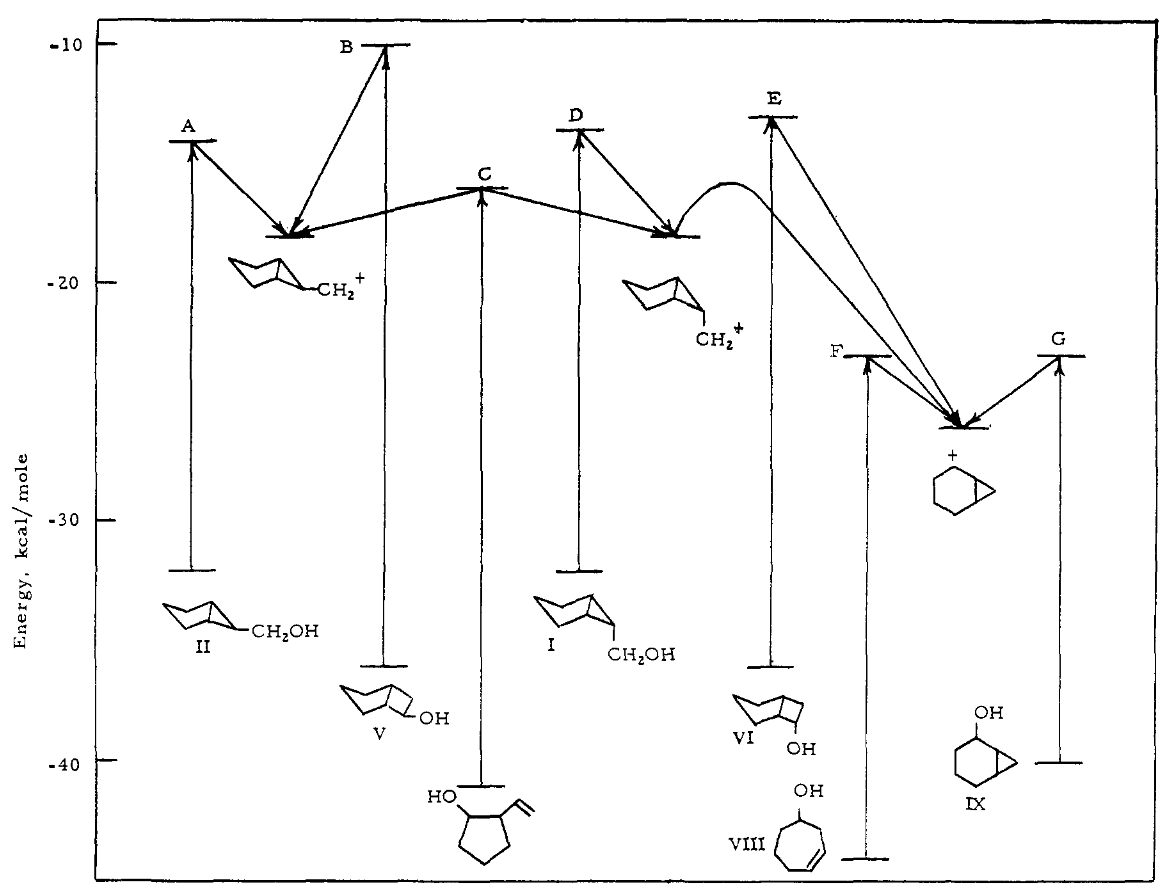

Figure 1. Relative energies of reactants and of activated complexes for acetolysis of C_7 derivatives.

could reclose to the *exo*-bicyclo[3.1.0]hexane-6-carbonium ion. Since this does not occur, it appears that the double bond is not free to rotate and is probably still bonded to the ring. While there may be a "homoallylic" vinylcyclopentyl cation, it is simplest to suppose the 2-vinylcyclopentyl products come from the same ion as the bicyclo[3.1.0]hexane-6-methyl products.

It would be interesting to compare the energies of the activated complexes formed in the acetolysis reactions. Table III summarizes the rate data and activation parameters for the set of compounds discussed here. In the cases for which $\Delta H^{\ddagger}$ was not available, it was estimated to be about 1 kcal/mole less than $\Delta F^{\ddagger}$. The heats of formation of the reactants are not known, but the values for the corresponding alcohols may be estimated from the Franklin group equivalents,[18] with a correction for the strain energies of the component rings (6.2 kcal/mole for a cyclopentane ring, 26.1 kcal/mole for a cyclobutane ring, and 27.5 kcal/mole for a cyclopropane ring). This method gives satisfactory results with bicyclo[3.1.0]hexane and bicyclo[2.1.0]pentane.[19]

Table III. Rates of Acetolysis of Isomeric C_7 Tosylates at 25°

Tosylate	$k \times 10^8$, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu	$\Delta F^{\ddagger}$, kcal/mole	Ref
exo-Bicyclo[3.2.0]-heptyl-6	7.7	26.3	−3	27.2	14
trans-2-Vinyl-cyclopentyl	43	24.9	−4	26.3	
endo-Bicyclo-[3.2.0]heptyl-6	5.3×10^3	23.2	0	23.3	14
3-Cyclohepten-1-yl	2.6×10^4	21.3	−3	22.3	
endo-Bicyclo-[3.1.0]hexane-6-methyl	1.1×10^6	18.4	−6	20.1	
exo-Bicyclo-[3.1.0]hexane-6-methyl	1.3×10^6	18.8	−4	20.0	
endo-2-Norcaranyl	$\sim 2 \times 10^8$			~15	*a*
exo-2-Norcaranyl	$\sim 4 \times 10^8$			~15	*a*

[a] Estimated from the data of ref 8.

Figure 1 was constructed using the above data, making the assumption that the heats of solution would be the same for all compounds, and that the conversion of an alcohol to a tosylate would give an enthalpy change which was independent of structure. Thus, these factors should simply shift the energy scale. The vertical lines correspond to the observed activation energies. The energies of the three cations are placed at an arbitrary distance below the corresponding activated complex.

The energies of the activated complexes A and D are of course about the same since the activation energies were essentially the same. The energy of C is also the same within the uncertainty of the estimation, but B is probably of higher energy. This is reasonable since V must undergo a rearrangement to form the cyclopropylcarbinyl cation.

It would appear that the 2-norcaranyl cation must be about 8 kcal/mole lower in energy than the bicyclo-

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[18] J. L. Franklin, *Ind. Eng. Chem.*, 41, 1070 (1949).

[19] The heat of formation of bicyclo[3.1.0]hexane is +12.4 kcal/mole (D. P. Konovolov, *Compt. Rend.*, **183**, 40 (1926)), and that for bicyclo-[2.1.0]pentane is +36.6 kcal/mole (R. B. Turner, "Kekule Symposium," Butterworth & Co., Ltd., London, 1959, p 67).

[3.1.0]hexane-6-methyl cation, accounting for the preferential rearrangement to the former. The two allylcarbinyl activated complexes, C and F, have energies close to those of the corresponding cyclopropylcarbinyl derivatives, suggesting that the structures of C and F may be close to those of A, D, and G, respectively. All of the energies appear quite reasonable, except for that of E. If the ionization process involves rearrangement to the norcaranyl ion, it is surprising that the energy of the activated complex is so much higher than that derived from VIII or IX. This point will receive further study.

We believe that this type of an analysis of solvolytic processes is of value, and we are currently determining the heats of formation of key compounds so that the uncertainties in the energy diagram may be minimized.

Finally, the high reactivity of 4-cycloheptenyl tosylate as compared to, for example, 3-cyclohexenyl tosylate should be considered. It would appear that the conformations available for the cyclohexene ring do not permit good orbital overlap between the π orbital of the double bond and the developing positive charge (Figure 2). However, the added flexibility of the cycloheptene ring permits this type of orbital overlap.

Bicyclo[2.1.0]pentane-5-methyl Tosylates

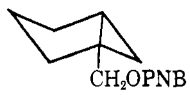
The rates of solvolysis were determined using standard techniques. The data for acetolysis and for ethanolysis are recorded in Tables IV and V. As in the previous case, the rate constants and activation parameters are essentially the same for the two isomers. Also, the values of m and **N** indicate the reactions to be limiting solvolyses.

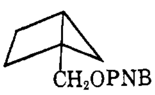
Table IV. Acetolysis of Bicyclo[2.1.0]pentane-5-methyl Tosylates

Tosylate	Temp, °C	Internal return, %	$k \times 10^4$,[a] sec^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu
exo	17.0	20	1.35 ± 0.01	21.1	−3
	32.0		8.6 ± 0.2		
endo	17.0	38	1.17 ± 0.01	21.0	−4
	32.0		7.45 ± 0.25		
Cyclopropylcarbinyl[b]	17.0	33	0.10	21.8	−2

[a] The rate constants are the average of two determinations; the deviation given is one-half the difference between the two rate constants. [b] See footnote *b*, Table I.

The rates of reaction are somewhat less than those for the bicyclo[3.1.0]hexane-6-methyl tosylates. If the central bond were involved in the ionization step, a rate increase would have been expected in view of the increase in strain energy on going from the bicyclohexanes to the bicyclopentanes. These results stand in contrast to the rates of solvolysis of bicyclo[3.1.0]hexane-1-methyl[20] and bicyclo[2.1.0]pentane-1-methyl[21] p-nitrobenzoates. Here, the effect of the difference in strain energy is seen in the rates of reaction. Clearly, the 1,2 and 1,3 cyclopropane bonds participate in stabilizing the cationic center, but the 2,3 bond is not significantly involved.





rel *k* 1 500

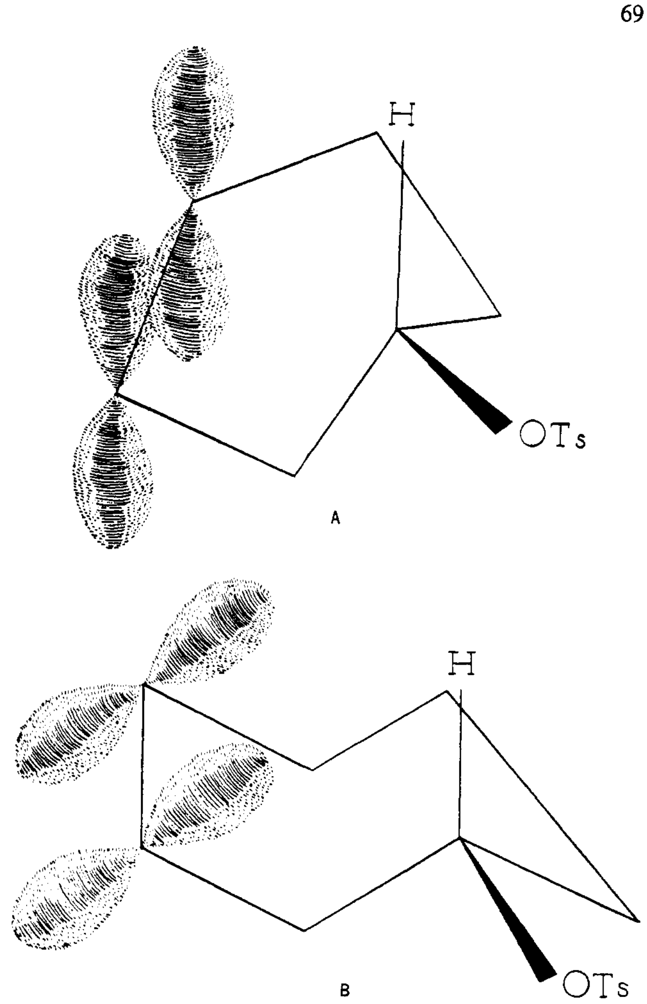


Figure 2.

The decrease in rate of solvolysis on going from the bicyclo[3.1.0]hexane-6-methyl tosylates to the bicyclo[2.1.0]pentane-5-methyl tosylates appears to be the general effect of increasing strain in the bridging ring, as can be seen from the data in Table VI. The effects of 1,2 and 2,3 bridging of the cyclopropane ring may be understood in terms of molecular orbital theory. This has been discussed by us elsewhere.[22]

The solvolysis of *exo*-bicyclo[2.1.0]pentane-5-methyl tosylate led to 20% of a reactive internal return product and 80% of acetates. The nmr spectrum of the internal return product indicated that it probably was 2-vinylcyclobutyl tosylate. Thus, aside from the tosyl protons, one could recognize the three protons of a vinyl group along with one proton adjacent to oxygen (τ 4.0–5.8) with a pattern similar to that of 2-vinylcyclopentyl tosylate, an allyl proton (τ 6.8–7.3) and diffuse absorption from τ 7.8 to 8.8 due to the cyclobutane methylene protons. An attempted synthesis from vinyllithium and cyclobutene epoxide failed.

The rate of acetolysis of the internal return product was determined at 32°, $k = 2.5 \times 10^{-5}$ sec^{-1}. This is 14 times the rate observed for cyclobutyl tosylate.[23]

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[20] W. D. Closson and G. T. Kwiatkowski, *Tetrahedron*, **21**, 2779 (1965).

[21] W. D. Dauben and J. Wiseman, *J. Am. Chem. Soc.*, **89**, 3545 (1967).

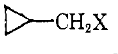
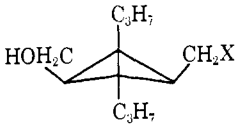
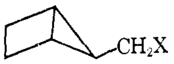
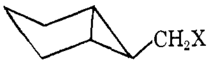
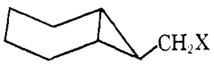
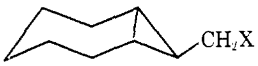
[22] K. B. Wiberg, *Tetrahedron*, in press.

[23] J. D. Roberts and V. C. Chambers, *J. Am. Chem. Soc.*, **73**, 5034 (1951).

Table V. Ethanolysis of Bicyclo[2.1.0]pentane-5-methyl Tosylates at 17°

Tosylate	% EtOH	Y	Internal return, %	$k \times 10^4$, sec^{-1}	m	N
exo	95	−1.287		2.39 ± 0.08	0.74	0.89
	80	0.0	7.5	21.6 ± 0.2		
endo	95	−1.287		0.82 ± 0.01	0.73	0.42
	80	0.0	38	7.10 ± 0.05		
Cyclopropylcarbinyl					0.75	1.07

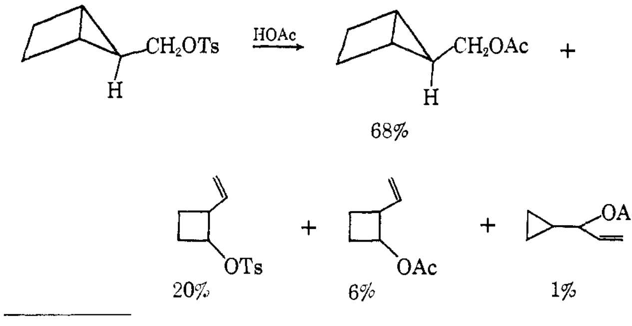
Table VI

	k_{rel}		
	X = OTs HOAc	X = ODNB 60% acetone	Ref
	1	1	8
	0.6		*a*
	1.2		
	82	40	8
		220	8
		51	8

[a] R. Breslow and P. Wolff, unpublished results; P. Wolff, Ph.D. Thesis, Columbia University, 1965.

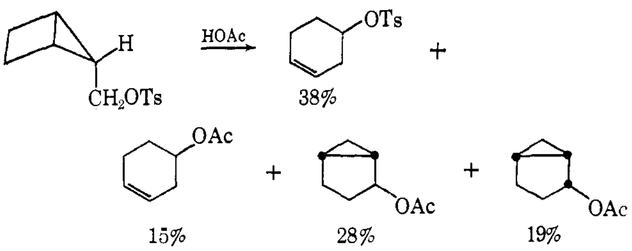
The major product (68%) from the acetolysis was found to be the parent acetate. Two other acetates also were found. One (6%) had an nmr spectrum corresponding to that of the internal return product and is probably 2-vinylcyclobutyl acetate. The other (1%) had an nmr spectrum showing both vinyl and cyclopropyl protons, suggesting vinylcyclopropylmethyl acetate. This structure was confirmed by an independent synthesis from divinylcarbinol and the Simmons–Smith reagent[24] followed by treatment with acetyl chloride.

When the acetolysis products were allowed to stand in acetic acid long enough so that the internal return product reacted, the concentration of the minor acetate increased considerably. It was independently shown that it was the major product from the solvolysis of 2-vinylcyclobutyl tosylate. This reaction is similar to the conversion of 2-methylcyclobutylamine to methylcyclopropylcarbinol on deamination.[25]



The major alcohol product from the ethanolysis of *exo*-bicyclo[2.1.0]pentane-5-methyl tosylate was the parent alcohol (90%). No vinylcyclopropylcarbinol could be detected.

The acetolysis of *endo*-bicyclo[2.1.0]pentane-5-methyl tosylate gave 38% internal return to 3-cyclohexenyl tosylate. The acetates could not be separated by vpc, but on conversion to the alcohols separation could be effected. Three alcohols were found in a ratio of 45:25:30 in order of retention time on a 1,2,3-tris(2-cyanoethoxy)propane column. They corresponded to *exo*-bicyclo[3.1.0]hexan-2-ol, 3-cyclohexen-1-ol, and *endo*-bicyclo[3.1.0]hexan-2-ol.



Ethanolysis gave four alcohols in the ratio 39:23:24:14. They were identified as *exo*-bicyclo[3.1.0]hexan-2-ol, 3-cyclohexen-1-ol, *endo*-bicyclo[3.1.0] hexan-2-ol, and *endo*-bicyclo[2.1.0]pentane-5-methanol.

These results are completely analogous to those for the bicyclo[3.1.0]hexane-6-methanols. The *exo*-tosylate of both series gave similar types of products: primarily parent acetate with the corresponding allylcarbinyl tosylate and acetate. Both are unable to rearrange to the 2-northujanyl (or 2-norcaranyl) system because of geometry. Further, both appear to form a carbonium ion which is similar to the parent tosylate in structure. Similarly, the *endo*-tosylates lead largely to the more stable 2-northujanyl or 2-norcaranyl ion, and aqueous ethanol is able to trap part of the initially formed ion leading to unrearranged product. Here again, it appears that the ion initially formed is structurally similar to the corresponding reactant.

It would be interesting to compare the results from the bicyclo[2.1.0]pentane-5-methanols with those for the corresponding bicyclo[2.2.0]hexyl-2 tosylates. Unfortunately, data are available only for the *exo* compound. McDonald and Reineke found that the *exo* isomer reacted with a rate constant extrapolated to 17° of 6×10^{-8} sec^{-1}.[26] The products were 55% *exo*-bicyclo[2.1.1]hexyl-5 tosylate and approximately equal amounts of *exo*-bicyclo [2.1.1]hexyl-5 acetate and 3-cyclohexenyl tosylate.

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(24) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **80**, 5323 (1958); *ibid.*, **81**, 4256 (1959).

(25) M. S. Silver, M. J. Caserio, H. E. Rice, and J. D. Roberts, *ibid.*, **83**, 3671 (1961).

(26) R. N. McDonald and C. E. Reineke, *ibid.*, **87**, 3020 (1965).

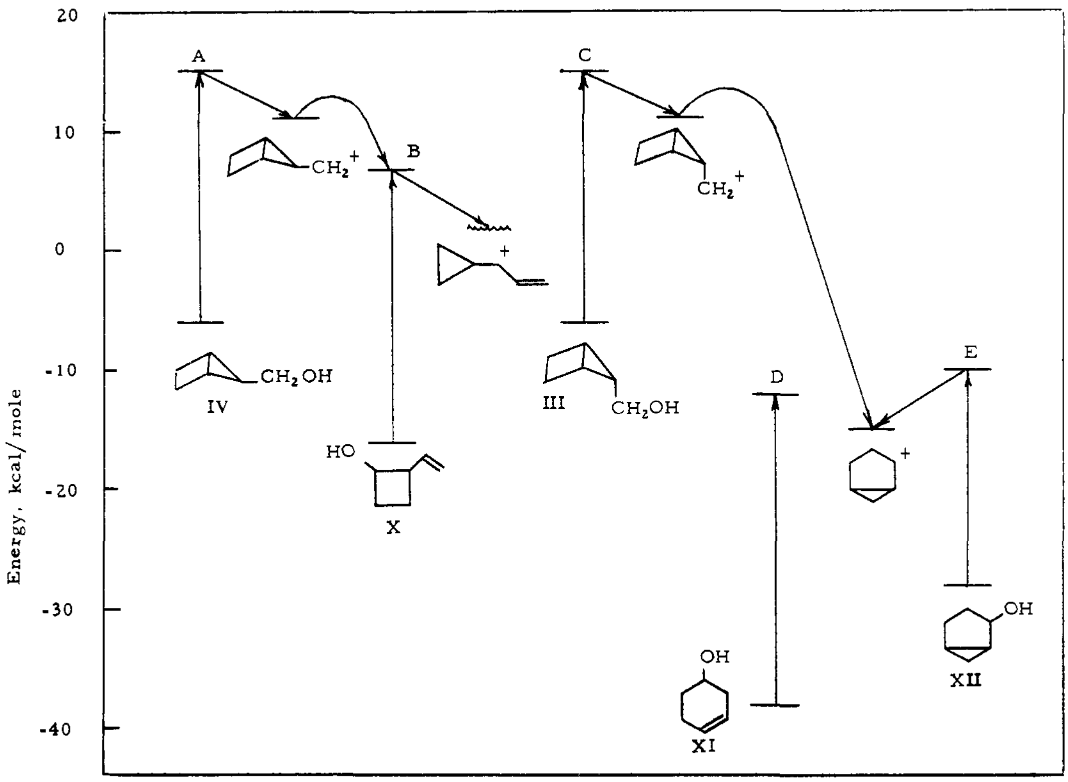
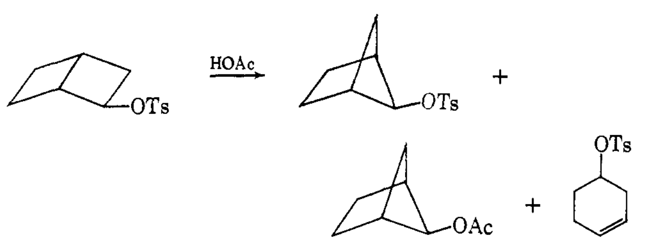


Figure 3. Relative energies of reactants and of activated complexes for acetolysis of C_6 derivatives.



The reason for lack of cyclobutyl participation is probably the same as for *exo*-bicyclo[3.2.0]heptane-6 tosylate; such participation would lead to a *trans*-fused northujanyl ion. Cyclobutylcarbinyl participation is probably favored over rearrangement to the bicyclo[2.1.0]pentane-5-methyl ion because of the greater strain relief in the former case.

Table VII. Rate of Acetolysis of Isomeric C_6 Tosylates at 25°

Tosylate	$k \times 10^8$, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu	$\Delta F^{\ddagger}$, kcal/mole	Ref
3-Cyclohexenyl	6	~26	...	27.3	*a*
exo-Bicyclo-[2.2.0]hexyl-5	9	24.7	−8	27.1	26
trans-2-Vinyl-cyclobutyl	1.3×10^3	~23		24.1	
endo-Bicyclo-[2.1.0]hexane-5-methyl	3.2×10^4	21.0	−4	22.2	
exo-Bicyclo-[2.1.0]hexane-5-methyl	3.7×10^4	21.1	−3	22.1	
endo-2-Nor-thujyl	6.5×10^6	~18	...	19.1	*a*
exo-2-Nor-thujyl	7.0×10^6	~18	...	19.0	*a*

[a] Private communication, Professor S. Winstein.

The kinetic data relating to the C_6 isomers are summarized in Table VII. Again, the heats of formation of the starting alcohols have been estimated leading to the energy diagram shown in Figure 3. Here, the energy of B is considerably lower than that of A. Correspondingly, the solvolysis of the tosylate of X gives very little III or IV, but rather allylcyclopropylcarbinyl derivatives. The energies of D and E are comparable, but the structure of the ion formed is not clear since the tosylate of XI gives largely 3-cyclohexenyl derivatives as products. Data about one of the most interesting compounds, *endo*-bicyclo[2.2.0]hexyl-2-tosylate, are not as yet available.

Experimental Section[27]

***endo*-Bicyclo[3.1.0]hexane-6-methanol.** A solution of 10 g (0.091 mole) of *endo*-bicyclo[3.1.0]hex-2-ene-6-methanol[28] in 100 ml of ethyl acetate was hydrogenated using 100 mg of Adam's catalyst and about 2 atm hydrogen pressure. The catalyst was filtered off and the ethyl acetate removed under reduced pressure. The remaining material was distilled giving 7.7 g (75%) of *endo*-bicyclo-[3.1.0]hexane-6-methanol, bp 79–85° (9 mm). The material was further purified by preparative vpc using a silicone column at 160°.

Anal. Calcd for $C_7H_{12}O$: C, 75.0; H, 10.8. Found: C, 75.0, 75.1; H, 10.8, 10.9.

The 3,5-dinitrobenzoate was prepared and recrystallized from ethanol giving the derivative with mp 102.5–103.8°.

***endo*-Bicyclo[3.1.0]hexane-6-methyl Acetate.** Excess acetyl chloride (5 g) was added dropwise with swirling to an ice-cold solution of 1.0 g of *endo*-bicyclo[3.1.0]hexane-6-methanol in 30 ml of dry pyridine. After standing for 15 min, 10 ml of water was added dropwise with swirling. The solution was extracted three times with 50-ml portions of pentane. The pentane solution was washed

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[27] Nmr spectra were determined using a Varian A-60 spectrometer and carbon tetrachloride solutions. Nmr spectra of the key alcohols are contained in the thesis of A. J. A. Melting points are corrected; boiling points are uncorrected.

[28] J. Meinwald, S. S. Labana, L. L. Labana, and G. H. Wohl, Jr., *Tetrahedron Letters*, 1789 (1965).

twice with dilute sulfuric acid and three times with aqueous sodium bicarbonate solution and dried over potassium carbonate. Distillation gave 0.9 g (65%) of the acetate, bp 45° (10 mm). The nmr spectrum had bands at τ 5.95 (d, J = 7 Hz, 2 H), 8.0 (s, 3 H), and 7.8–9.2 (m, 9 H).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.1; H, 9.2. Found: C, 70.4, 70.5; H, 9.4, 9.4.

endo-**Bicyclo[3.1.0]hexane-6-methyl Tosylate.** To a cold (−10°) solution of 1.5 g (1.34 mmoles) of *endo*-bicyclo[3.1.0]hexane-6-methanol in 100 ml of dry ether was added 2.93 g (1.53 mmoles) of *p*-toluenesulfonyl chloride. The mixture was stirred mechanically while portions of powdered potassium hydroxide (3 g) were added over a 30–60-min period. The cold solution was stirred for 4 hr, and then kept in a refrigerator at 10° for 2 days.

To the reaction mixture was added 75 g of ice water and ice, and the layers were separated. The aqueous layer was extracted with two 50-ml portions of ether and this was added to the organic solution. The latter was washed with water and dried over potassium carbonate. Removal of the ether in the cold using a rotary evaporator gave 4 g of yellow-white crystals. It was important to keep the material cold since a few minutes at room temperature converted it to a black tar. Two recrystallizations from ether–pentane gave 2.5 g of white crystals, mp 41.5°. The material was stored in Dry Ice. The nmr spectrum had bands at τ 2.5 (A_2B_2, 4 H), 5.95 (d, J = 7.5 Hz, 2 H), 7.6 (s, 3 H), and 8.09–9.2 (m, 9 H).

exo-**Bicyclo[3.1.0]hexane-6-methanol.** Ethyl bicyclo[3.1.0]-hexane-6-carboxylate (10 g, 0.065 mole, 4:1 *exo*/*endo*) in 50 ml of ether was added dropwise to 3 g (0.08 mole) of lithium aluminum hydride in 400 ml of ether. The addition required 30 min, after which stirring and refluxing were continued for 1 hr. Water was added to destroy excess lithium aluminum hydride. The ether layer was decanted and was dried over anhydrous potassium carbonate. Distillation gave 3.6 g (50%) of bicyclo[3.1.0]hexane-6-methanol (4:1 *exo*/*endo*), bp 63° (2 mm).

The above mixture (35 g) was separated by preparative vpc using a silicone column at 160° giving the pure (>99%) *exo* isomer. The *endo* isomer was contaminated with a few per cent of the *exo* isomer and was not used.

Anal. Calcd for $C_7H_{12}O$: C, 75.0; H, 10.8. Found: C, 75.0, 74.9; H, 10.7, 10.8.

The 3,5-dinitrobenzoate was prepared from the *exo* isomer and after three recrystallizations from ethanol it had mp 117.2–118.2°.

exo-**Bicyclo[3.1.0]hexane-6-methyl Acetate.** Excess acetyl chloride (2.5 g) was added to a cold solution of *exo*-bicyclo[3.1.0]-hexane-6-methanol in 10 ml of pyridine. After 15 min, the reaction mixture was diluted with water and extracted with pentane. After washing with dilute sulfuric acid and with sodium bicarbonate solution, the pentane layer was dried over anhydrous potassium carbonate. Removal of the solvent gave the acetate which was purified by vpc. The nmr spectrum had bands at τ 6.2 (d, J = 7.5 Hz, 2 H), 8.03 (s, 3 H), and 8.1–9.25 (m, 9 H).

Anal. Calcd for $C_9H_{14}O_2$: C, 70.1; H, 9.2. Found: C, 69.9; 70.1; H, 9.1, 9.3.

exo-**Bicyclo[3.1.0]hexane-6-methyl Tosylate.** *exo*-Bicyclo[3.1.0]-hexane-6-methanol (2.0 g, 0.018 mole) and 3.4 g (0.018 mole) of *p*-toluenesulfonyl chloride were dissolved in 150 ml of dry ether in a 300-ml flask equipped with a drying tube and a magnetic stirrer. The solution was cooled to −10° and portions of powdered potassium hydroxide (4 g) were added over a period of 1 hr. The mixture was allowed to stir overnight at 0°.

Ice water was added and the ether layer was separated and dried over anhydrous potassium carbonate. Removal of the ether in the cold left an oil which was added to pentane and cooled to Dry Ice temperature giving some crystals. These were used as seeds in subsequent recrystallizations. The recrystallization was accomplished from ether–pentane at −20 to −30° giving white crystals of *exo*-bicyclo[3.1.0]hexane-6-methyl tosylate, mp 10–12°. The nmr spectrum had bands at τ 2.45 (A_2B_2, 4 H), 6.2 (d, J = 7.5 Hz, 2 H), 7.6 (s, 3 H), and 8.1–9.3 (m, 9 H).

Copper-Catalyzed Addition of Ethyl Diazoacetate to Cyclobutene. Eighty grams (1.48 moles) of cyclobutene, 25 g (0.22 mole) of ethyl diazoacetate, and 1 g of electrolytic copper powder were placed in a 300-ml, high-pressure Parr bomb. The bomb was sealed at Dry Ice temperature and was rocked and heated to 80° for 5 hr. The bomb was allowed to cool to room temperature and then was cooled with Dry Ice. The reaction product was distilled through a Dry Ice cooled trap to recover unreacted cyclobutene (70 g). The residue was combined with that of two other runs on the same scale. Distillation gave 27 g (30%) of volatile material, bp 45° (1 mm). Vpc analysis (Carbowax column) indicated it to be a mixture of diethyl fumarate and ethyl bicyclo[2.1.0]pentane-5-carboxylate. A sample of the latter was collected for analysis.

Anal. Calcd for $C_7H_{10}O_2$: C, 68.5; H, 8.6. Found: C, 68.5, 68.5; H, 8.4, 8.4.

Bicyclo[2.1.0]pentane-5-methanol. The mixture obtained above (20 g, 0.143 mole) was added to 5.2 g (0.133 mole) of lithium aluminum hydride in 500 ml of ether. The addition required 30 min and was followed by heating to reflux for 30 min. Excess water was added, and the ether layer was separated by decantation. The aqueous layer was extracted with ether and ether solutions were combined and dried over anhydrous potassium carbonate. Distillation gave 7 g (50%) of bicyclo[2.1.0]pentane-5-methanol, bp 65–70° (4 mm). The isomers could be separated by vpc using a silicone column at 130°. The *exo* isomer had a 10-min retention time whereas the *endo* isomer had an 11-min retention time. The *exo*/*endo* ratio was 85:15.

Photolytic Addition of Ethyl Diazoacetate to Cyclobutene. Cyclobutene (112 g, 2.08 moles) and 15 g (0.13 mole) of ethyl diazoacetate were placed in a small irradiation flask equipped with a quartz well. A 500-w Hanovia lamp with a Corex filter was placed in the well and a Dry Ice condenser with a drying tube was connected to the flask. Dry Ice cooled methanol was circulated through the cooling jacket of the well. The solution was irradiated for 20 hr, after which 10 g (0.088 mole) of ethyl diazoacetate was added and the photolysis continued for an additional 15 hr. The reaction mixture had turned a brownish yellow. Distillation gave 78.5 g of recovered cyclobutene and 28 g of higher boiling material. The product from two runs was combined and distilled giving 24 g (37%) of a colorless oil, bp 45° (1 mm).

The oil was reduced with lithium aluminum hydride (5 g) as described above giving 12.5 g (75%) of a colorless oil, bp 65–70° (4 mm). Separation was effected by vpc using a silicone column at 160°. Two olefinic products, retention times 4.75 and 5.0 min, formed 38% of the mixture. They were not further investigated. *exo*-Bicyclo[2.1.0]pentane-5-methanol, retention time 6.0 min, formed 36 % of the mixture, while the remainder (26%) was the *endo* isomer, retention time 6.5 min.

Anal. Calcd for $C_6H_{10}O$ (*endo*): C, 73.4; H, 10.2. Found: C, 73.2, 73.0; H, 10.1, 10.0. Calcd for $C_6H_{10}O$ (*exo*): C, 73.4; H, 10.2. Found: C, 73.6, 73.4; H, 10.0, 10.2.

exo-**Bicyclo[2.1.0]pentane-5-methyl Acetate.** *exo*-Bicyclo[2.1.0]-pentane-5-methanol (0.5 g) was added to excess acetyl chloride in pyridine. The ester was isolated as above giving 0.6 g of the acetate, which was purified by vpc. The nmr spectrum had bands at τ 6.35 (d, J = 7.5 Hz, 2 H), 7.7–8.1 (m, 2 H), 8.1 (s, 3 H), and 8.2–8.9 (m, 5 H).

Anal. Calcd for $C_8H_{12}O_2$: C, 68.5; H, 8.6. Found: C, 68.3, 68.1; H, 8.7, 8.9.

exo-**Bicyclo[2.1.0]pentane-5-methyl Tosylate.** *exo*-Bicyclo[2.1.0]-pentane-5-methanol (2 g, 0.02 mole) and 3.8 g (0.02 mole) of *p*-toluenesulfonyl chloride were dissolved in 200 ml of freshly dried ether. To the cooled (−10°) solution was added with stirring 4 g of powdered potassium hydroxide in portions. The reaction mixture was treated as described above giving a yellow oil which crystallized on standing at −80°. Recrystallization from ether–pentane gave 3.3 g (64%) of colorless *exo*-bicyclo[2.1.0]pentane-5-methyl tosylate, mp 14.6°. The nmr spectrum had bands at τ 2.5 (A_2B_2, 4 H), 6.3 (d, J = 7.5 Hz, 2 H), 7.6 (s, 3 H), and 7.8–9.0 (m, 7 H).

endo-**Bicyclo[2.1.0]pentane-5-methyl Tosylate.** The tosylate was prepared from 1.28 g of *endo*-bicyclo[2.1.0]pentane-5-methanol, 2.5 g of *p*-toluenesulfonyl chloride, and 2.5 g of potassium hydroxide as described above. Recrystallization from ether–pentane gave 1.8 g of the tosylate, mp 41–42°. The nmr spectrum had bands at τ 2.5 (A_2B_2, 4 H), 5.75 (d, J = 7.5 Hz, 2 H), 7.6 (s, 3 H), and 7.8–9.1 (m, 7 H).

3-Cyclohepten-1-ol. To a mixture of 8 g (0.02 mole) of lithium aluminum hydride and 14 g (0.1 mole) of aluminum chloride in 750 ml of dry ether contained in a flask fitted with a mechanical stirrer, reflux condenser with drying tube, and an additional funnel was added 50 g (0.45 mole) of 3,4-epoxycycloheptene dropwise with rapid stirring. A vigorous exothermic reaction ensued, and the addition required about 1 hr. The solution was stirred and heated with a water bath for 30 min. The excess hydride was destroyed by *cautious* addition of water. The ether layer was decanted and the residue was washed with ether. The combined ether fractions were dried over magnesium sulfate and distilled giving 35 g (70%) of 3-cyclohepten-1-ol, bp 80–85° (15 mm). The product had spectra identical with that of the material prepared by the method of

Cope, *et al.*, which involves reduction of the corresponding ketone.[29] The nmr spectrum had bands at τ 4.1–4.7 (m, 2 H), 5.8 (s, moves on dilution, 1 H), 6.3–6.8 (m, 1 H), and 7.6–8.9 (m, 8 H).

3-Cyclohepten-1-yl Tosylate. A solution of 10 g (0.09 mole) of 3-cyclohepten-1-ol in 150 ml of pyridine was cooled in ice for about 15 min. Then, 23.8 g (0.125 mole) of *p*-toluenesulfonyl chloride was added with swirling. After standing in a refrigerator overnight, the mixture was poured into 150 ml of cold water and extracted with three 100-ml portions of ether. The ether extracts were washed successively with 10% hydrochloric acid, 10% sodium bicarbonate solution, and saturated salt solution. After drying over anhydrous magnesium sulfate, the ether was removed using a rotary evaporator giving a yellow oil. The oil crystallized after washing with pentane giving 21 g (88%) of colorless 3-cycloheptenyl tosylate. After recrystallization from ether–pentane, it had mp 33–34°. The nmr spectrum had bands at τ 2.5 (A_2B_2, 4 H), 3.9–4.8 (m, 2 H), 5.4–5.95 (m, 1 H), 7.6 (s, 3 H), and 7.5–8.9 (m, 8 H).

***exo*- and *endo*-2-Norcaranol.** A mixture of *exo*- and *endo*-2-norcaranyl acetates was prepared by the method of Cope, *et al.*,[12] and was reduced with lithium aluminum hydride to give the norcaranols, bp 75° (15 mm). They could be separated by vpc using a Carbowax column at 150°. The *exo* isomer had a retention time of 11.5 min, and the *endo* isomer had a retention time of 10.0 min. The nmr spectrum of the *exo* isomer had bands at τ 5.5 (moves on dilution, 1 H), 5.9–6.2 (m, 1 H), 8.0–9.2 (m, 8 H), 9.25–9.65 (m, 1 H), 10.0–10.25 (m, 1 H). The nmr spectrum of the *endo* isomer had bands at τ 5.85 (s, moves on dilution, 1 H), 5.85–6.15 (m, 1 H), 7.7–9.2 (m, 8 H), and 9.3–9.8 (m, 2 H).

***exo*- and *endo*-2-Northujanols.** The *endo* isomer was prepared by the reaction of methylene iodide and zinc with cyclopenten-3-ol. Equilibration was effected by the procedure of Corey[30] and Hanack[31] giving a 64:36 *exo*:*endo* ratio. This is in agreement with Hanack's results, but not with Corey who appears to have the numbers reversed.

***trans*-2-Vinylcyclopentanol.** A 2.44 *N* solution of vinyllithium[32] in tetrahydrofuran (82 ml) was placed in a flask equipped with a stirrer, nitrogen inlet tube, additional funnel, and drying tube and which had been swept out with nitrogen. Cyclopentene oxide (25.2 g, 0.3 mole) was added dropwise with stirring, and the reaction mixture was stirred overnight under nitrogen. Excess water was added; the layers were separated. The aqueous layer was extracted with three 100-ml portions of ether and these were combined with the organic layer. The ether solution was washed with saturated salt solution and dried over anhydrous magnesium sulfate. Distillation gave 5.0 g of recovered cyclopentene oxide and 1 g (4.4%) of *trans*-2-vinylcyclopentanol, bp 70° (25 mm). The major product was a viscous nonvolatile oil.

Anal. Calcd for $C_7H_{12}O$: C, 75.0; H, 10.8. Found: C, 75.1, 74.9; H, 10.9, 10.8.

The alcohol was converted to the 3,5-dinitrobenzoate which had mp 56–57.5° after recrystallization from ethanol–water. It was also converted to the acetate with acetyl chloride and pyridine. The nmr spectrum had bands at τ 4.1–4.65 (m, 1 H), 5.0–5.5 (m, 3 H), 7.6–7.8 (m, 1 H), 8.2 (s, 3 H), and 8.2–8.6 (m, 6 H).

***trans*-2-Vinylcyclopentyl Tosylate.** *trans*-2-Vinylcyclopentanol (1.0 g, 0.009 mole), 1.7 g (0.009 mole) of *p*-toluenesulfonyl chloride, and 10 ml of pyridine were mixed in a small flask and stored at 0° for 24 hr. The reaction mixture was treated with 50 g of ice-water, and extracted with three 50-ml portions of ether. The ether solution was washed with dilute acid, sodium bicarbonate solution, and saturated salt solution. After drying over anhydrous copper sulfate, the solvent was removed giving 2.0 g of *trans*-2-vinylcyclopentyl tosylate which resisted all attempts at crystallization. The nmr spectrum had bands at τ 2.45 (A_2B_2, 4 H), 4.1–4.7 (m, 1 H), 4.9–5.6 (m, 3 H), 7.2–7.65 (m, 1 H), 7.6 (s, 3 H), and 7.85–8.8 (m, 6 H).

Reaction of Bicyclo[3.1.0]hexane-6-methanols with Formic Acid. Bicyclo[3.1.0]hexane-6-methanol (*exo*:*endo* = 4:1) (10 g, 0.089 mole) was dissolved in 200 ml of 97% formic acid containing 4 g of *p*-toluenesulfonic acid. After standing overnight, the reaction mixture was poured into a mixture of ice and excess potassium hydroxide. The solution was extracted with three 250-ml portions of ether. Removal of the solvent gave 7.5 g (75%) of a clear oil, bp 58–64° (20 mm). Vpc analysis indicated it to contain 80% *trans*-2-vinylcyclopentanol and 20% 3-cyclohepten-1-ol.

Cyclopropylvinylmethanol. Zinc–copper couple was prepared by the method of Schechter and Shank.[33] Methylene iodide (107 g, 0.4 mole) was added to 35 g (0.54 mole) of zinc–copper couple in a flask equipped with a mechanical stirrer, an addition funnel, and a reflux condenser with a drying tube. After 30 min, 84 g (1 mole) of divinylcarbinol was added dropwise with stirring. An exothermic reaction occurred. The solution was heated to reflux for 30 min after the addition was completed.

The reaction mixture was filtered, then added to 10% hydrochloric acid. The ether layer was separated and the aqueous layer was extracted with ether. The combined ether layers were washed with sodium bicarbonate solution, then dried over anhydrous potassium carbonate. The ether was removed through a Vigreux column. Distillation of the residue gave 50 g of recovered divinylcarbinol, bp 100–120°, and a mixture of cyclopropylvinylmethanol (42%), methylene iodide, and divinylcarbinol (10 g). This was separated by preparative vpc giving the pure alcohol.

Anal. Calcd for C_6H_{10}: C, 73.4; H, 10.2. Found: C, 73.4, 73.5; H, 10.1, 10.3.

The alcohol was converted to the acetate in the usual fashion. The nmr spectrum had bands at τ 4.0–5.6 (m), 8.0 (s), and 8.8–9.8 (m).

Product Determinations. a. Acetolysis of *exo*-Bicyclo[3.1.0]hexane-6-methyl Tosylate. *exo*-Bicyclo[3.1.0]hexane-6-methyl tosylate (5.3 g, 0.02 mole) was taken up in 250 g of a 0.09 *M* solution of potassium acetate in dry acetic acid. The solution was allowed to stand for 30 min at 25°. It was added to 1 l. of water which was then extracted with three 200-ml portions of pentane. These pentene extracts were washed with excess aqueous sodium bicarbonate, then dried over anhydrous magnesium sulfate. The pentane solution was distilled through a small Vigreux column, and the nmr spectrum of the residue was taken. This indicated a vinyl group, a tosyl group, an acetoxymethyl group, and the carbinyl protons of *exo*-bicyclo[3.1.0]hexane-6-methyl acetate.

A pot-to-pot distillation (1 mm) using a water bath (70°) separated the mixture into a distillate (0.9 g) and a residue (1.5 g). The distillate was subjected to vpc analysis (10 ft × 0.25 in. Carbowax column, 160°). There were only two components in 47:53 ratio with retention times of 3.0 and 4.75 min, respectively. The first was shown to be *trans*-2-vinylcyclopentyl acetate by comparison with spectra of an authentic sample. The second was similarly shown to be *exo*-bicyclo[3.1.0]hexane-6-methyl acetate.

The residue from the distillation resisted attempts at recrystallization. Its nmr spectrum showed it to be *trans*-2-vinylcyclopentyl tosylate. The amount of internal return was 50%.

b. *endo*-Bicyclo[3.1.0]hexane-6-methyl Tosylate. The reaction of 3 g (0.011 mole) of *endo*-bicyclo[3.1.0]hexane-6-methyl tosylate in 500 ml of acetic acid containing excess potassium acetate was allowed to proceed, and was worked up as described above. The volatile products were poorly resolved on a variety of vpc columns, and the mixture was reduced to alcohols using lithium aluminum hydride. The alcohols were separated on a 10 ft × $^3/_8$ in. Carbowax column giving four components in the ratio 18:60:18:4. Each was identified by comparison of spectra with those of authentic samples; they were found to be *trans*-2-vinylcyclopentanol, *endo*-2-norcaranol, *exo*-2-norcaranol, and *endo*-bicyclo[3.1.0]hexane-6-methanol, respectively.

The tosylate residue was cleaved to the corresponding alcohols using the method of Denny and Goldstein.[34] The product was separated by vpc using a tris(β-cyanoethoxy)propane column at 160°. Only two components were found and they were identified as *trans*-2-vinylcyclopentanol and 3-cyclohepten-1-ol.

c. *exo*-Bicyclo[2.1.0]pentane-5-methyl Tosylate. The reaction of 6.5 g (0.025 mole) of *exo*-bicyclo[2.1.0]pentane-5-methyl tosylate in 500 ml of acetic acid containing excess potassium acetate was allowed to proceed for 120 min at 32°. The reaction mixture was worked up as described above. The volatile product was separated by vpc using a Carbowax column giving five components in the ratio 4.7:2.2:7.8:1.6:84. The major component was bicyclo[2.1.0]pentane-5-methyl acetate. The 7.8% isomer was found to be 2-vinylcyclobutyl acetate and the 2.2% component was vinylcyclopropylmethyl acetate. The nmr spectrum of the tosylate residue corresponded to that expected from 2-vinylcyclobutyl tosylate.

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d. ***endo*-Bicyclo[2.1.0]pentane-5-methyl Tosylate.** The samples of *endo*-bicyclo[2.1.0]pentane-5-methyl tosylate used in the kinetic runs were put in excess potassium acetate after titration. The solutions were worked up as described above. The nonvolatile material solidified on cooling and was shown to be 3-cyclohexen-1-yl tosylate by comparison with an authentic sample. The volatile materials could not be separated by vpc and therefore were reduced to alcohols with lithium aluminum hydride. The alcohols could be separated on a 12 ft × 1/8 in. tris(β-cyanoethoxy)propane column at 120°, and were found to have a 45:25:30 ratio with retention times of 10.5, 11.5, and 12.3 min, respectively. The first and third were *exo*- and *endo*-2-northujanols and the second was 3-cyclohexen-1-ol.

e. ***trans*-2-Vinylcyclopentyl Tosylate.** The reaction of 2.7 g (0.01 mole) of *trans*-2-vinylcyclopentyl tosylate in 300 ml of dry acetic acid containing excess potassium acetate was allowed to proceed for 16 hr at 70°. The reaction mixture was worked up as indicated above, and in this case no internal return product was found. The product could be separated by vpc using a tris(β-cyanoethoxy)propane column at 160° giving four components in the ratio 29:25:31:15 with retention times of 4.25, 4.5, 6.25, and 7.75 min, respectively. The first two components were *trans*- and *cis*-2-vinylcyclopentyl acetates; the third component was *exo*-bicyclo[3.1.0]hexane-6-methyl acetate and the fourth component was a mixture of *exo*- and *endo*-2-norcaranyl acetates (1:4 mixture, infrared spectrum).

f. Ethanolysis. The ethanolysis experiments were carried out using 50% ethanol which was 0.5 *M* in base. After a time corresponding to ten half-lives, the reaction mixtures were worked up in essentially the same fashion as the acetolysis experiments. The alcohols formed were identified by vpc separation and comparison of spectra with those of authentic samples, giving the data cited in the text.

Kinetic Experiments. Acetolysis. Acetic acid (reagent grade) was dried by heating with a small excess of acetic anhydride, and the amount of the latter was determined by the method of Bruckenstein.[35] Typically, the concentration was about 0.05 *M*. Standard potassium acetate solution was prepared by dissolving weighed quantities of reagent grade anhydrous potassium carbonate in measured amounts of acetic acid. *p*-Toluenesulfonic acid solutions were prepared by dissolving approximately weighed quantities of reagent *p*-toluenesulfonic acid in acetic acid. The solutions were standardized by titration with the potassium acetate solution.

The reactive tosylates were studied as follows. The tosylate was weighed into a 5-ml volumetric flask, and carbon tetrachloride was added to the mark. The solution was kept at 0°. A number of test tubes were placed in a constant-temperature bath. Each was filled with measured amounts (0.1, 0.2, 0.3 ml etc.) of potassium acetate solution. To this was added five drops of bromphenol blue indicator and sufficient dry acetic acid to bring the volume to 10.0 ml. With a 250-μl Hamilton syringe, a 200-μl aliquot of the carbon tetrachloride solution was added to one of the test tubes. Immediately after injection, a timer was started. The solution was stirred vigorously. The timer was stopped and the time recorded when the yellow color of the indicator had disappeared. The procedure was repeated with each of the tubes.

The less reactive tosylates were studied by sealing 4-ml aliquots containing excess potassium acetate into ampoules. The ampoules were placed in a constant-temperature bath, and at selected intervals one was removed and quickly cooled. A 3-ml aliquot was removed and was titrated with *p*-toluenesulfonic acid solution to the bromphenol blue end point.

In each case, the rate constant was determined from a plot of $\ln (V_\infty - V)$ against time. Two determinations were made for each compound and each temperature, and the rate constants generally agreed to better than ±5%.

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Concerning the Mechanism of Single-Bond Shortening. Evidence from the Crystal Structures of 1-Biapocamphane, 1-Binorbornane, and 1-Biadamantane[1]

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Abstract: The $J_{^{13}\mathrm{CH}}$ at the bridgehead carbon in norbornane is 139 Hz, indicating 28% s character. Using this number, the Dewar plot of bond length against s character (length = 1.692 − 0.0062% s) predicts a central bond length in 1-binorbornane of 1.517 A. We find this bond length to be 1.515 ± 0.005 A. We therefore agree with Dewar that the concepts of conjugation or hyperconjugation are not necessary to explain single-bond lengths in compounds such as butadiene, styrene, or propylene. A correction for two H···H repulsions in 1-binorbornane reduces the central bond length to about 1.503 A and strengthens the case against conjugation in nonaromatic hydrocarbons.

In recent years there has been considerable controversy over the effect of attached groups on carbon–carbon single-bond lengths.[2] The controversy concerns the relative importance of resonance, hybridization, and nonbonded repulsions in causing the variation observed among C–C single-bond lengths in unsaturated molecules like butadiene, biphenyl, and propylene. Stated in its simplest form, the observed fact is that lengths of C–C single bonds increase as the number (*N*) of atoms attached to the bonded carbons increases,[3,4] as shown in Table I. Similarly, heats of formation or heats of hydrogenation indicate that energies of the single bonds in this series undergo a parallel decrease.[5–7] Three different explanations have been offered.

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