Tetrahedron, 1966, Suppl. 8, Part II, pp. 399–420. Pergamon Press Ltd. Printed in Great Britain

NUCLEOPHILIC REACTIVITY OF THE CARBON–CARBON DOUBLE BOND—V

ACETATES AND OLEFINS OF THE HYDRINDANE SERIES BY THREE π ROUTES COMPARED WITH TWO σ ROUTES

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Abstract—The acetolysis of 3-(Δ^2-cyclohexenyl)propyl *p*-nitrobenzenesulfonate (**11**) is 1·64 times as fast as that of its saturated analog, the 3-cyclohexylpropyl ester; it leads to a mixture including 18·9% of bicyclic products, which consist of olefins (3 or 4) and acetates (2) in the ratio of 1·67 to 1. The product is closely related in composition to that obtained[7] by acetolysis of the toluenesulfonate (**14**) of 9-bicyclo(3.3.1)nonanol, except for a threefold lower proportion of olefins (characteristic of the π route) and greater stereospecificity in the acetates.

The acetolysis of *trans*-2-(2-vinylcyclopentyl)ethyl *p*-nitrobenzenesulfonate (**12**) is only 95% as fast as the saturated standard, and leads to 95% of unrearranged acetate, 5% of equatorial *trans*-4-hydrindyl acetate, and no olefins. The isomeric *p*-nitrobenzenesulfonate (**13**) of *cis*-2-(2-vinylcyclopentyl) ethanol undergoes acetolysis at a rate 5·78 times that of the saturated standard. The product is 76% bicyclic and contains four hexahydroindenes and four hydrindyl acetates in the olefin/acetate ratio of 0·39, twelve times lower than that in the σ route from **14**.

The solvolysis rates are rationalized in terms of the conformational barriers to be surmounted in the formation of the transition state, and are correlated with the fractions of bicyclic product formed. In line with earlier work, the olefin/acetate ratio in the product is regarded as an indication of the relative involvement of classical ion pairs in the reaction sequence, which is always less in the π route than in the σ route for reasons which are discussed. Differences in product compositions also require the occurrence of bridged ion pairs with different properties in the several cases.

The "π route"[1] to a reaction product is that in which a new bond is formed by nucleophilic attack of a carbon-carbon double bond or other π-bonded structure upon an ionizing center. Previous work[2b] has shown that the driving force, or acceleration traceable directly to the double bond, in the ionization of 2-(3,4-dimethyl-Δ^3-cyclopentenyl)ethyl *p*-nitrobenzenesulfonate (**1**) amounts to a factor of 3300, and hence that the ring closure is a true intramolecular displacement by the double bond, not a two-step process initiated by unassisted ionization. The similar rate increments of 5- to 7-fold brought about by the first and second methyl groups spoke for a high degree of symmetry in the attack of the double bond upon the ionizing center and indicated that the transition state in the ionization had not developed any appreciable localization of positive charge at either end of the double bond in the monosubstituted

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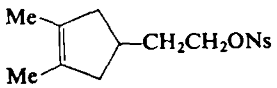
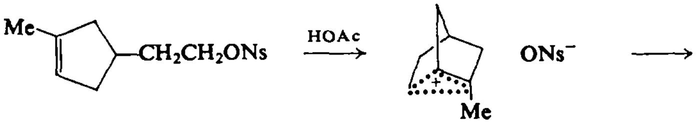
[1] S. Winstein and P. Carter, *J. Amer. Chem. Soc.* **83**, 4485 (1961).

[2] [a] P. D. Bartlett, S. Bank, R. J. Crawford and G. H. Schmid, *J. Amer. Chem. Soc.* **87**, 1288 (1965);
[b] P. D. Bartlett and G. D. Sargent, *Ibid.* **87**, 1297 (1965);
[c] P. D. Bartlett, W. D. Closson and T. J. Cogdell, *Ibid.* **87**, 1308 (1965);
[d] P. D. Bartlett, W. S. Trahanovsky, D. A. Bolon and G. H. Schmid, *Ibid.* **87**, 1314 (1965).

starting material 2. At the same time a comparison of the effects of methyl groups on the double bond and at position 1 of the sulfonate led to the conclusion[2a] that the transition state bears more positive charge at the carbon atoms of the original double bond than at the carbon atom from which the anion departed. These results were all consistent with the view that the initial product of the ionization, toward which the transition state represents the most direct approach, is a bridged or "nonclassical" ion of the norbornyl type (3). Some of the stereospecificities observed[3] in multiple ring closures are also in best accord with this view.



1



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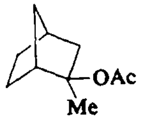

ONs ≡ $O_3SC_6H_4NO_2$ (p)

If cyclization by the π route, through inherent characteristics of the process, involves a compulsory passage through a bridged ion which may not be characteristic of other modes of ionization, a way lies open for comparison of the properties of classical and nonclassical ions in borderline cases. Such comparisons have been made a number of times by using deamination as a source of model classical ions, but the conditions are often so different from those of solvolysis that one may be changing a number of significant variables at once.[4-6] In the solvolysis of the *p*-nitrobenzenesulfonates of cyclohexanol (4), 5-hexenol (6), and cyclopentylmethanol (5) the products in each case include cyclohexene (7) and cyclohexyl acetate (8), whose total and relative amounts were accurately determined.[2c] It was concluded that the classical cyclohexyl cation (9) is much more prone to yield cyclohexene than is the bridged ion (10) which must occur in common in the conversion of 5 or 6 to cyclohexyl products. Since the results from 5 were intermediate between those of 4 and 6, it was noted that an intimate ion pair containing the bridged ion 10 would not be identical when coming from the two sources: 5 would lead to an ion pair (10a) with the sulfonate anion favorably located for internal return to cyclohexyl *p*-nitrobenzenesulfonate while the ion pair (10b) formed in the π route has its anion located at a distance from either carbon atom with which it must combine to form the cyclohexyl sulfonate.

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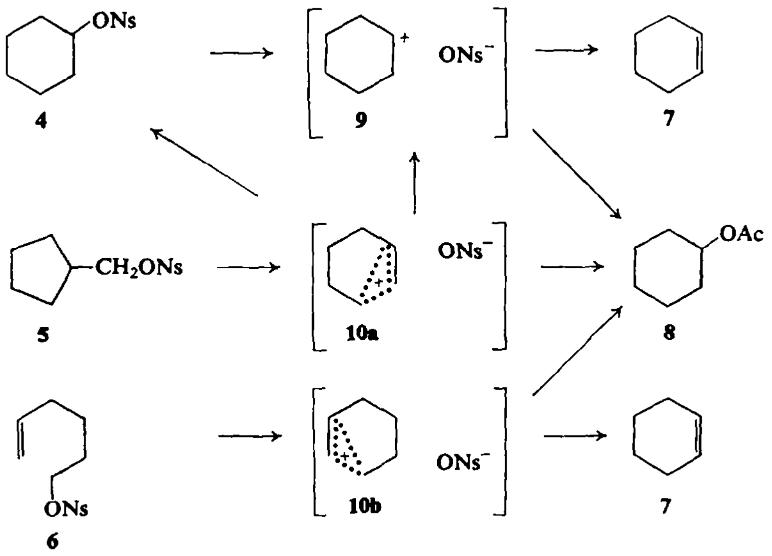
[3] See [a] W. S. Johnson and J. K. Crandall, *J. Org. Chem.* **30**, 1785 (1965), and Refs cited there; also [b] W. S. Johnson, P. J. Neustaedter and K. K. Schmiegel, *J. Amer. Chem. Soc.* **87**, 5148 (1965).

[4] E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry and R. Winter, *J. Amer. Chem. Soc.* **85**, 169 (1963).

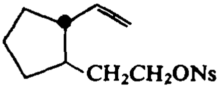
[5] J. A. Berson and A. Remanick, *J. Amer. Chem. Soc.* **86**, 1749 (1964).

[6] P. D. Bartlett, *Nonclassical Ions*, pp. 463, 465, 492. Benjamin, New York (1965).



The present report represents a further inquiry into the differing properties of ion pairs generated in different ways. We have examined the rates and products of solvolysis in acetic acid of 3-(Δ^2-cyclohexenyl)propyl *p*-nitrobenzenesulfonate (**11**), *trans*-2-(2-vinylcyclopentyl)ethyl *p*-nitrobenzenesulfonate (**12**), and *cis*-2-(2-vinylcyclopentyl)ethyl *p*-nitrobenzenesulfonate (**13**). The comparison of the rates of these solvolyses is relevant to the conclusion[2d] that the energy barrier to solvolytic ring closure includes contributions from all the eclipsed interactions involved as the molecule passes from its most populated conformation to the transition state. The product compositions by these three π routes gain interest by comparison with two σ routes to

11



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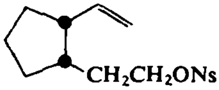
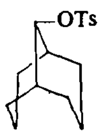
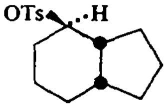


13

the same series of products[7] by the acetolysis of 9-bicyclo(3.3.1)nonyl tosylate (**14**) and *cis–exo*-4-hydrindyl tosylate (**15**).



14



15

Preparation of compounds. The cyclohexenylpropyl compound **11** was prepared according to Chart I and the isomeric 2-(2-vinylcylopentyl)ethyl compounds were obtained as shown in Chart II.

[7] [a] C. S. Foote and R. B. Woodward, *Tetrahedron* **20**, 687 (1964);
[b] C. S. Foote, Thesis, Harvard (1961).

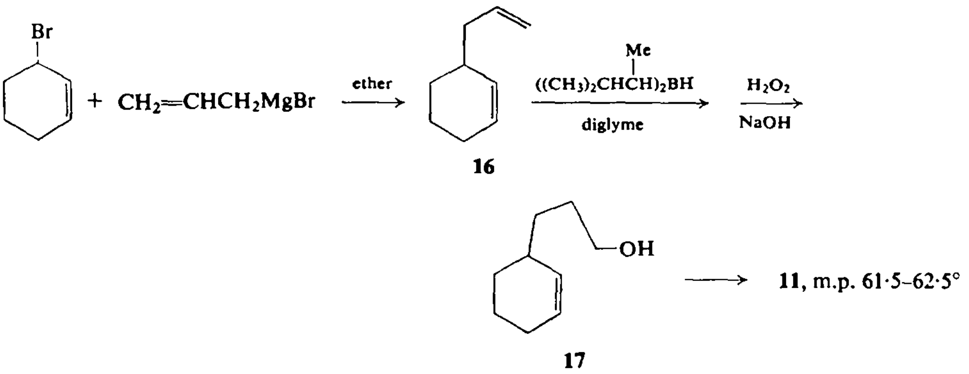


CHART I

The acetate from **17** and the *p*-nitrobenzenesulfonate and acetate of the related saturated alcohol were prepared as reference compounds. The isomeric alcohols **24** and **25** were separated by preparative vapor phase chromatography on a Carbowax 20 M column at 160°. The acetates of **24** and **25** were prepared from these alcohols; other reference compounds were prepared by known methods as described in the Experimental.

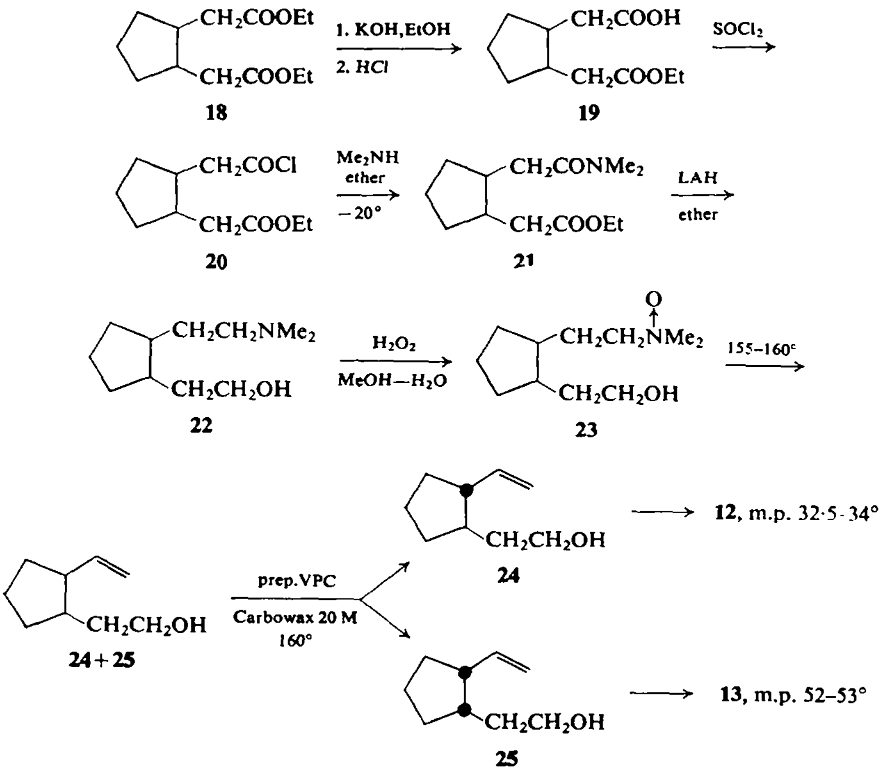


CHART II

TABLE 1. ACETOLYSIS PRODUCTS OF SULFONATES **11**, **12** and **13** in Presence of 0·2M SODIUM ACETATE

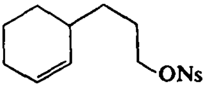
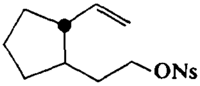
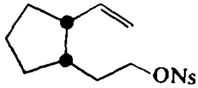
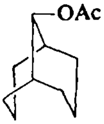
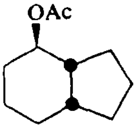
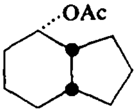
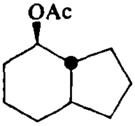
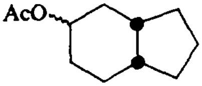
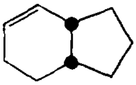
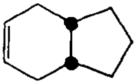
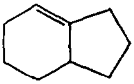
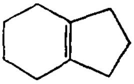
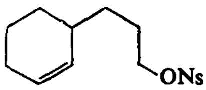
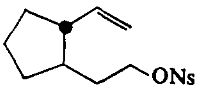
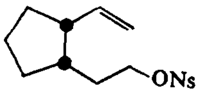
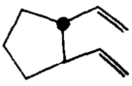
Starting material		 **11**	 **12**	 **13**
Conc., M		0·154	0·1	0·1
Temp		100°	94°	75·5°
Time, no. of half-lives		16	6	6
Products:				
	**34**	1·5		
— 7 	**35**	5·2, 5·6		18
	**36**			21
	**37**		5	9·4
	**38**			2
	**39**	11·8, 12·3[a]		6·6
	**40**			2·1
	**41**			3·7
	**42**			7·3

TABLE I—*continued*

Starting Material Products:	 **11**	 **12**	 **13**
Uncyclized	81·1, 82·6	95	23·6
Other		 tr.	Unknown HC 1·5

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[a] The VPC of the hydrocarbon fraction from **11** on UCON LB 550X at 125° was similar to that of the hydrocarbons from **14**.[7b] The two major peaks at 46·6 and 50·0 min were those identified by Foote as *cis*-Δ^4-hexahydroindene and Δ^8-hexahydroindene, but were present in the ratio of 3·5 : 1 instead of 2·1 : 1 as found from **14**. A shoulder corresponding to $\Delta^{4(8)}$-hexahydroindene was present as in Foote's product, but Δ^5-hexahydroindene, if present, would probably not have been rsolved under these conditions. These indications were used in preparing the comparative figures in Table 2. We thank Professor R. B. Woodward for providing samples of the solvolysis mixture and several of the compounds described in Ref. 7.

Products of acetolysis. The *p*-nitrobenzenesulfonates **11**, **12** and **13** were solvolyzed in acetic acid in the presence of excess sodium acetate to neutralize strong acid. The resulting solutions were diluted with water, extracted with pentane, and separated by distillation into a hydrocarbon fraction and a higher boiling acetate fraction. Each fraction was subjected to VPC at column temperatures from 75 to 165°, on one or more of five different columns. In each identification the retention time was compared with that of an authentic sample and, when conditions of optimum separation had been worked out, samples were isolated for NMR and IR characterization. Table 1 lists the product compositions from the three *p*-nitrobenzoates, and Table 2 compares the product distributions in the *cyclized* products from these three π routes and from the σ routes from **14** and **15**.[7] Viewed broadly, the products from **11** resemble those from **14** and **15**, as would be expected if **11** and **14** yield the same bridged ion with, in the case of **14**, internal return to **15**.[7] The *trans*-vinylcyclopentane, **12**, affords only 5% of cyclic product, a fact consistent with the high strain involved in any interaction of its ionizing center with its vinyl group; the cyclic product from **12**, in contrast to all other cases, consists of a single acetate, **37**, uniquely derivable from the bridged ion **28**. The *cis* cyclopentane **13** gives 76·4% of cyclic product which consists of a mixture of four olefins and four acetates with the latter predominating. These product compositions are discussed in detail below.

Solvolysis rates. Each *p*-nitrobenzenesulfonate was solvolyzed over a range of temperature in the presence of excess sodium acetate, the rates being followed titrimetrically in the case of **11** and conductimetrically in the cases of **12** and **13**. The rates for **11** were determined also in the absence of added salt. The results are reported in Table 3. In Table 4 a comparison is made of the rate constants at the common temperature, 79·5°, with the rate constant for the saturated analog, 3-cyclohexylpropyl

TABLE 2. DISTRIBUTION OF CYCLIZATION PRODUCTS FROM ACETOLYSIS OF FIVE SULFONATES

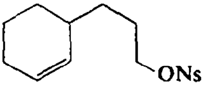
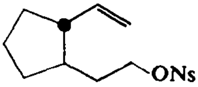
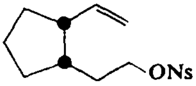
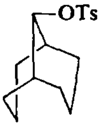
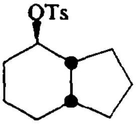
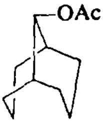
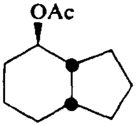
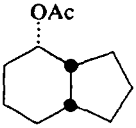
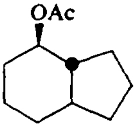
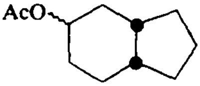
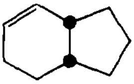
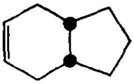
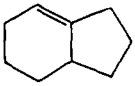
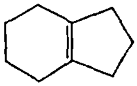
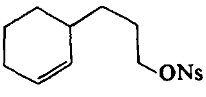
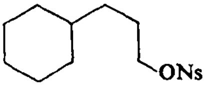
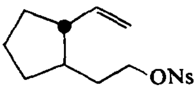
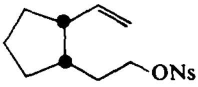
		a	*b*	*c*	*d*	*e*
		 **11**	 **12**	 **13**	 **14**	 **15**
Products:						
	**34**	7·9			5	2
	**35**	29·6		25·2	8	
	**36**			29·4	3	
	**37**		100	13·1	0·4	
	**38**			2·8		
	**39**	44·8		9·2	51·5	44
	**40**			2·9		

TABLE 2—*continued*

 **41**			5·2		
Unidentified	~5		2·0	6·7	21
 **42**	12·7		10·2	24	33
(olefins)/(acetates)	1·67	0	0·39	5·0	50

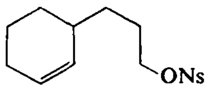
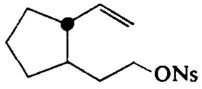
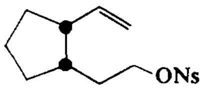
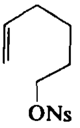
[a] 100°, 16 half-lives, 1·30 equiv of NaOAc.
[b] 94°, 6 half-lives, 2·0 equiv of NaOAc.
[c] 75·5°, 6 half-lives, 2·0 equiv of NaOAc.
[d] 80–85°, 8–11 half-lives, 0·35 equiv of KOAc.[7]
[e] 65°, 10 half-lives, 1·15 equiv of KOAc.[7]

TABLE 3. RATES OF ACETOLYSIS OF **11**, **12** AND **13**

Compound	Conc., M	(NaOAc), M	Temp (°)	$10^5\,k$ sec^{-1}
 **11**	0·01	0·03	79·4	2·17
	0·01	0	100·65	12·5, 11·9
	0·01	0·03	100·65	15·8, 16·4
	0·01	0	109·52	25·4, 25·8
	0·01	0	119·62	59·6, 57·0
	0·01	0·03	119·62	70·5, 71·4
 **43**	0·01	0	79·4	1·03, 1·02
	0·01	0·03	79·4	1·32, 1·32
	0·01	0	100·85	6·77, 6·79
	0·01	0·03	100·85	9·42, 9·46
	0·01	0	119·62	30·7, 30·8
	0·01	0·03	119·62	41·7, 40·5
 **12**	0·02	0·03	80·12	1·31, 1·29
			98·33	7·23, 7·32
			113·00	24·8, 25·8
 **13**	0·02	0·03	79·68	7·43, 7·42
			98·33	45·7, 44·8
			113·00	142·5, 148·0

p-nitrobenzenesulfonate. As in previous instances[2a, c, d] there is reasonable correspondence between the apparent degree of participation of the double bond, as inferred from rates, and the proportion of ring closure seen in the solvolysis products, in further support of the conclusion that ring closure is an essential part of the process by which the double bond accelerates solvolysis.

TABLE 4. RELATIVE ACETOLYSIS RATES AT 79·5° AND ACTIVATION PARAMETERS

Compound	$10^5 k_U$[a]	k_U/k_S[b]	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ e.u./mole
 **11**	2·17	1·64	22·8	−15·4
 **12**	1·26	0·95	23·5	−14·6
 **13**	7·63	5·78	23·3	−11·7
 **6**	2·25[c]	1·49	23·1	−14·7

[a] k_U = rate constant for unsaturated compound, at 79·5°, in 0·03 M NaOAc.

[b] k_U/k_S = rate constant relative to saturated standard of comparison. **43** is taken as the saturated standard for all compounds, $k_S = 1{\cdot}32 \times 10^{-5}$ sec^{-1}.

[c] (NaOAc) = 0·0355 M[2c]:

DISCUSSION

Rates of solvolysis. In Part IV of this series[2d] it was concluded that, among similarly substituted double bonds in the 5,6-position to a departing anion, the rate of assisted solvolysis is determined by the conformation barriers between the most favored conformation of the starting material and the transition state. The design of the substrates **11**, **12** and **13** was intended to test this idea further by comparison with **6**.

In **11** the double bond is *cis*-disubstituted; this feature might be expected to increase the rate by a factor of about 2·5 over 5-hexenyl *p*-nitrobenzenesulfonate (**6**).[8] This effect might be offset by limitations imposed on the rotation about the 1,2-single bond in the ring. In other respects **6** and **11** are closely comparable; both must surmount two ethane-like rotational barriers and a third barrier which, in **6**, is like that of propylene and in **11** corresponds to a relatively easy equatorial-to-axial change on the cyclohexene ring. The fact that the rates and activation parameters for the acetolysis of **6** and **11** are closely similar was therefore to be expected.

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[8] [a] P. D. Bartlett and E. M. Nicholson, forthcoming publication;
[b] E. M. Nicholson, thesis, Harvard University (1965).

Compound **13** is closely comparable with **6** except that one of the conformational barriers is eliminated by the *cis* configuration at the cyclopentane ring. Partially offsetting this is the constraint which the five-membered ring places on the transition state, in which the preferred dihedral angle at the ring junction is not known. As indicated in Table 4, the free energy of activation for **13** is more favorable than that for **6** by 1·2 kcal/mole, compared to the 2·8 kcal/mole which might be foreseen from the difference of a single eclipsing barrier.

Attention should be called, however, to the lack of usefulness of overall activation parameters as determined for compounds of this type, as far as mechanistic interpretations are concerned. From the ratios in the third column of Table 4 we conclude that up to one-third of the reaction is proceeding through internal displacement by the π electrons of the double bond, while the rest is proceeding solvolytically and by direct displacement by outside acetate ion. The activation parameters should be determined separately for each mechanism by resolving the reaction rate at each temperature into at least these three components. Such a resolution is possible in principle, but the determinations by difference which are involved would set extraordinarily severe requirements of precision on the rate measurements. Thus in the case of **12**, where the activation parameters for the pure π-mechanism would be of great interest, they cannot be determined because the reaction is dominated by the 95% which goes without participation of the double bond.

In the case of *n*-hexyl *p*-nitrobenzenesulfonate at 79·5°, where the rate constant in acetic acid is $1{\cdot}0 \times 10^{-5}$ sec^{-1}, the rate constant is increased to $1{\cdot}50 \times 10^{-5}$ by an average concentration during the run of 0·026M sodium acetate. This is a greater effect than that shown by 0·03 M lithium perchlorate ($k = 1{\cdot}29 \times 10^{-5}$).[2c] Since lithium perchlorate is usually much more effective than sodium acetate with respect to its kinetic salt effect on the acetolysis of sulfonate esters,[9] the implication is clear that the acceleration by sodium acetate is largely by superposing a direct S_N2 displacement upon the solvolysis. Such a conclusion is also consistent with the fact that the effects of sodium acetate upon the acetolysis rates of a number of saturated primary *p*-nitrobenzenesulfonates are very much alike,[8b] and lead to a rate constant $k(S_N2) = 15{\cdot}5 \times 10^{-5}$ sec^{-1} at 80°. If we use this as a basis for estimating the S_N2 components of the rates measured, and use an average sodium acetate concentration during each run, we obtain the figures given in Table 5 for the total solvolytic and assisted solvolytic rate constants, k_U(solv) and k_U(asstd). In Part III[2c] we considered alternative ways of estimating the unassisted components of the solvolyses from measurements of the solvolysis rates of the saturated analogs of the substrates. In *trans*-2-vinylcyclopentylethyl *p*-nitrobenzenesulfonate (**12**) we have the most sensitive detector to date for this quantity, for there is just 5% of cyclic product from this substrate. If we calculate the fraction of assisted solvolysis under the conditions of the product study, as in Table 5, using the assumption that the unassisted solvolysis rate of the unsaturated compound is 76% of that of the saturated compound (one of the two values considered in Part III[2c]), then the calculated fraction of assisted solvolysis f_A (column 6 of Table 5) is the same for **12** as the observed fraction of cyclic product (column 7). If we use the fraction 0·87 instead of 0·76, the calculated f_A is only one-third as great. The figure 0·76 yields a general parallel between f_A and percent cyclic product for the four entries of Table 5.

[9] A. H. Fainberg and S. Winstein, *J. Amer. Chem. Soc.* **78**, 2763 (1956).

TABLE 5. ESTIMATED ASSISTED SOLVOLYSIS RATE CONSTANTS AND ASSISTED FRACTION OF REACTION

		sec^{-1} × 10^5				
Compound	k_U	$k_U(S_N2)$[a]	k_U(solv)[b]	k_U(asstd)[c]	f_A(%)[d]	Per cent of bicyclic prod.
11	2·17	0·31	1·86	1·08	28·8	18·9
12	1·26	0·31	0·95	0·17	5·2	5
13	7·63	0·31	7·32	6·54	68	76
6	2·25	0·31	1·94	1·16	14	16·3

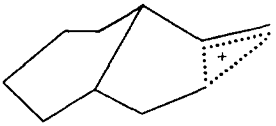
[a] Estimated as $k(S_N2)\dfrac{[\mathrm{NaOAc}]_0+[\mathrm{NaOAc}]_\infty}{2}$ in solvolysis.

[b] $k_U(\mathrm{solv})=k_U-k_U(S_N2)$.

[c] $k_U(\mathrm{asstd})=k_U(\mathrm{solv})-0{\cdot}76\,k_S=k_U(\mathrm{solv})-0{\cdot}78$.

[d] $f_A=\dfrac{k_U(\mathrm{asstd})}{k_U(\mathrm{solv})+15{\cdot}5\times10^{-5}([\mathrm{NaOAc}]_0+[\mathrm{NaOAc}]_\infty)/2}$ in product-study runs.

The ratio of 38·5 between the rates of assisted solvolysis of the *cis* and *trans* isomers 13 and 12 is greater than corresponds to the generally supposed difference in energies between *cis* and *trans* isomers of vicinally substituted cyclopentanes,[10] and thus indicates that the transition states in the π routes from these two sources are unequal in the direction of greater strain for the *trans*. This is of some interest in view of the fact that in the hexahydro- and octahydroindenes equilibrium generally favors the *trans* isomer over the *cis*;[11] the transition state in the assisted solvolysis therefore possesses some feature not inherent in either 1,2-disubstituted cyclopentanes or hydrindenes, favoring *cis* over *trans* configuration. The π-bridged transition states **26** to **29** should have a strain pattern more resembling that of the bicyclo(3.3.0)octanes, except for somewhat different interatomic distances between C_1 and the atoms of the original double bond.



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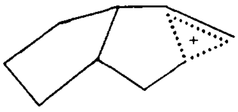

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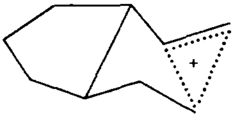

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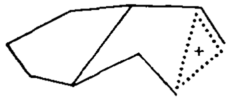

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Products. The separation of the products involved a selection of vapor chromatography columns, no one of which was capable of effecting complete resolution of the mixture. It is therefore necessary to inquire what are the limits of quantitative and

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[10] E. L. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, *Conformational Analysis*, p. 204. Interscience, New York (1965).

[11] Ref. 10, p. 230.

qualitative reliability in the product compositions. Since each product reported was isolated and characterized by IR and NMR spectra, we believe that the presence of each such product has been established. There are, however, other reasonable products which were not found, and the possibility remains that one or more of these may have been present and have escaped separation from the known components. Hexahydroindenes not observed include the *cis*- and *trans*-Δ^1, the Δ^3, the *trans*-Δ^4 and *trans*-Δ^5 isomers; missing hydrindyl acetates include all four 1-isomers, all three 2-isomers, the *cis*- and *trans*-8-isomers, the axial *trans*-4-isomer, and both *trans*-5-isomers, beside the fact that the configuration of the acetoxy group in the *cis*-5 acetate (**38**) was not established. Neither was it determined whether the ratio of products is dependent on temperature or on the time of standing under solvolytic conditions, although such a temperature dependence is suggested by the comparison in Table 6 of the hydrocarbon distributions[12] in the products from the related substrates **11**, **14** and **15**.

TABLE 6

	Hexahydroindenes, % of hydrocarbon fraction		
Source and Temp	Δ^4	Δ^8	Other
11, 100°	71·8	20·3	8
14, 80–85°[7]	62·2	29·2	8
15, 65°[7,12]	45	33·6	21·4

In view of these limitations we shall try to avoid over-interpretation of the present results by confining attention to the most conspicuous points of difference between the different π routes and σ routes.

First of all, the comparison of the products from **11**, **14** and **15** is especially instructive since the bridged ion **30** is the expected first product by the σ route from **14** and by the π route from **11**, and the classical ion **31**, expected from 15,[14] might be formed rapidly also from **30**.

The olefin/acetate ratio in the product is 1·67 from **11**, 5·9 from **14**, and 50 from **15**. If the product in the case of **15** is formed by way of the normal ion pair **31**-OTs, then at least 14% of the product from **14** and at least 35% of the product from **11** must have arisen by another path.

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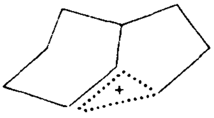
[12] The hydrocarbon product from **15** at 65° on further study is reported to contain, in addition to major amounts of the components identified by Foote and Woodward, and $\Delta^{4(8)}$-hexahydroindene, present in the product from **13**, also Δ^3-hexahydroindene,[13] which is believed to be absent in the product from **13**. It may be that the product from **15**, which solvolyzes ten times faster than **13**, had been exposed so relatively short a time to the solvolytic conditions as to allow the isolation of an early and unstable kinetic product.

[13] H. L. Goering, private communication.

[14] By applying the usual rate factor of **11** ($=k_{\mathrm{ONs}}/k_{\mathrm{OTs}}$) we find that k_{15}/k_{11}, reduced to the same leaving group, is of the order of 375. We thank Professor H. L. Goering for the information on the rate constant of acetolysis of **15**. Both this rate ratio and the failure of **15** to yield any appreciable product with the carbon skeleton of **14** support the idea that **15**, like cyclohexyl *p*-nitrobenzenesulfonate, ionizes to a classical ion which is stable relative to the bridged ion.

We have called attention previously[2c] to a general tendency for acetolysis via classical ions to yield higher olefin/acetate ratios than those involving bridged ions. Such differences are also observed when acetolysis of an arylsulfonate is compared with deamination of the related primary amine with nitrous acid or an alkyl nitrite. Since the acetolysis yields the higher olefin/acetate ratio, yet the deamination is believed to yield the ion with the most localized positive charge, the degree of "classicity," or charge localization, of the cation cannot be the fundamental criterion determining the competition between elimination and acetate formation. For example, at 80° the acetolysis of cyclohexyl *p*-nitrobenzenesulfonate yields cyclohexene and cyclohexyl acetate in a mole ratio of 6·7, while deamination of cyclohexylamine with isoamyl nitrite in acetic acid at the same temperature yields the ratio 0·57.[15] This ratio, and the ratio 0·51 between the same two products as obtained from cyclopentylmethylamine,[15] happen to be close to the 0·4 ratio previously[2c] concluded to be characteristic of the nonclassical ion pair **10b** as produced by the π route. What these two low-olefin reactions have in common is the absence of a stable anion in juxtaposition to the locus of positive charge in the immediate product of the rate-determining step. In the case of deamination the cation and anion are separated by the length of a nitrogen molecule; in the ion pair from the π route (**10b**) the anion is separated from the locus of positive charge by a CH_2-group which, experience shows, never breaks back out of its π involvement in product determination. We conclude that the proximity of the stable anion to the positive charge, and its ability to interact with a neighboring proton, may be very important in producing an elimination product despite the lack of nucleophilic character of the sulfonate anion. A similar role of the tosylate ion has been detected in the phenomenon of merged bimolecular substitution and elimination.[16] Thus we do not regard the olefin/acetate ratio in acetolysis as any fundamental index of localized or delocalized character of the cation, but as a resultant of some factors involving the position of the anion, and others involving the conformational requirements of the two transition states. It so happens that most positions of the anion which, by the above reasoning, are unfavorable for elimination are also favorable for displacement by acetic acid or acetate ion; also the conformations of the cation which are unfavorable for one can be favorable for the other. We therefore cannot even apportion the determination of the olefin/acetate ratio between factors specifically favorable to one product and those unfavorable to the other.



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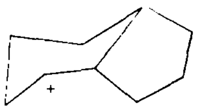

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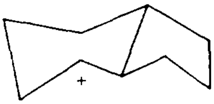

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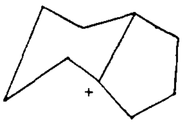

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[15] T. J. Cogdell, Thesis, p. 32. Harvard (1965).

[16] S. Winstein, D. Darwish and N. J. Holness, *J. Amer. Chem. Soc.* **78**, 2915 (1956).

It may be fortuitous that the well-stabilized bridged ion pair from the π route and the related, totally unstabilized, "hot" ion pair from the deamination yield olefins and acetates in the same ratio. There may, however, be a simple intrinsic reason for this. Many ionic reactions occur at diffusion-controlled rates, and this should be especially true of reactions of the reactive fragment from deamination. In the most probable conformation of the latter, as well as in the rigid, puckered form of a bridged ion, no six neighboring atoms will be coplanar as required for the most favorable approach to olefin formation. In the "hot" ion this dominates product formation because of the speed with which nucleophiles attack the electron-deficient carbon atom; in the bridged ion the reaction may be less rapid, but so are those conformational changes which must attend olefin formation. One role of the stable anion in the classical ion pair is to prolong the lifetime of the species, allowing conformational fluctuations to contribute to product determination.

An unsolved problem in the interpretation of the present results is to decide which differences in product composition indicate different structures of the intervening ions, and which may be explained by the substantial differences in anion location in the ion pair. In the following discussion we shall adopt the working hypothesis that, if a classical hydrindyl ion pair is produced, it survives long enough to behave the same regardless of its source, whether it reacts as a pair or as a free cation.

Sulfonates **11**, **14** and **15** are closely related—in the same way as **6**, **5** and **4**—in that the cyclized products are derivable from the first by the π route, from the second by the σ route to the same bridged ion, and from the third by unassisted ionization. With respect to positioning of the anion, the ion pair from **15** can hardly differ appreciably from that formed from **14**; it is therefore reasonable to attribute the extra acetates produced from **14** to product determination in the bridged-ion pair before its conversion into a classical ion pair. The unusually small amount of acetate from **15** is consistent with anion shielding on the *exo* side of **31** and steric hindrance to approach from the *endo* side. That **11** produces 35% of its product before formation of a hydrindyl ion pair is consistent with the unshielded situation of the ion **30** when formed by the π route.

Participation of the vinyl group in **12** and **13** in the ionization leads to bridged ions which cannot yield bicyclo(3.3.1)nonyl ester **14**, but can lead to the hydrindyl system. The *trans* vinyl compound **12** yields very little cyclized product, but what there is appears to be entirely equatorial 4-acetoxy-*trans*-hydrindane, (**37**), identical with Foote's material in its retention time on three VPC columns.[7] That there is undetectably little olefin suggests, in terms of our generalization, that the intermediate ion opens with unusual ease to the acetate. Two configuratively different bridged ions, **28** and **29**, are possible. Dreiding models show that **29**, which should open to the epimer of the observed product, has nonbonded hydrogen atoms at C_5 and C_8 (hydrindane numbering) which are only 1·75 Å apart, compared to 2·2 Å for the closest such approach in **28**, which should yield the product (**37**) actually observed. The classical *trans*-4-hydrindyl cation (**32**) is rigidly puckered and, if it intervened, might be expected to yield more acetates than its stereoisomers and to show a preference for **37**. In fact,[17] the products from equatorial *trans*-4-hydrindyl tosylate acetolysis at 60° include 82% of **37**, in contrast to the strong predominance of olefins from all the other hydrindyl

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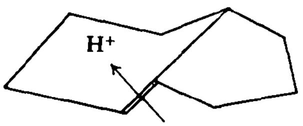
[17] H. L. Goering, private communication.

tosylates. Thus a minor amount of conversion of **28** to **32** during the solvolysis of 12 would not produce a large change in the nature of the product.

The *cis*-vinylcyclopentyl compound **13**, in addition to showing the most participation of the double bond in solvolysis, yields the most complex product, including four acetates and four olefins, with the former strongly predominating. Although stereospecificity is largely lacking, the pattern of hydrocarbons is not quantitatively that of either of the other two sources of hexahydroindenes, and from the limited amount of **39** it seems doubtful that any more than 25% of the product can be formed with intervention of the classical ion **31**. The presence of similar amounts of the *endo* and *exo*-4-acetoxyhydrindanes is in accord with indications from models that **26** and **27** should be formed with equal ease from **13**. Half of the products—two acetates and two olefins—cannot be formed without hydrogen shifts. Three of these might be pictured as arising from classical hydrindyl cations produced by hydride shifts in one direction or the other, as may well be the case in the solvolysis of **15**. There is a problem, however, with respect to equatorial 4-acetoxy-*trans*-hydrindane, formed as 13·4% of the cyclic product. In order to produce this from classical hydride shifts it would be necessary for **31** to isomerize to **33** and for this to return to **32**. But the direct acetolysis of *exo-cis*-4-hydrindyl toluenesulfonate, the σ route most likely to involve classical ions, produces 33% of Δ^8-hexahydroindene with only a total of 2% of acetates. If this exemplifies the behavior of **33**, this ion is surely not involved in a sequence resulting in 13·4% of the equatorial *trans*-4-acetate.

Thus, to explain the products from **13** we need not only the classical ions **31** and **32**, and the bridged ions **26** and **27**, but a type of intermediate having the properties of neither, and permitting a facile slippage from the *cis* to the *trans* hydrindane ring system. Except for the failure of **15** to exhibit the phenomenon, we might have attributed this isomerization to a migration of the bridge in **31**, thus interchanging the functions of the two rings and producing a mirror image of **32** as drawn above. A similar migration of C_8 in the bridged ion **26**, if it could occur, would likewise lead to a *trans*-4-hydrindyl cation. Such a reaction would be of the unusual type in which a three-center bond is broken into with retention rather than inversion at the carbon where the displacement occurs. A precedent exists in the *cis*-transannular internal return of *trans*-5-cyclodecen-1-yl *p*-nitrobenzoate to the *p*-nitrobenzoate of *trans-cis*-1-decalol.[18] An alternative way of converting the *cis*- to the *trans*-4-hydrindyl cation without passing through the 8-hydrindyl cation might be by way of the sequence **27**→**34**→**35**→**32**. An observation in harmony with the viability of **34** is that *endo–cis*-4-hydrindyl tosylate, despite imaginable steric hindrance to ionization, solvolyzes seven times as fast as the *exo* isomer.[7b] Again it is necessary to start with an ion other than **31** in order to avoid predicting products identical with those from **15**.



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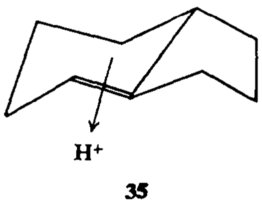

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[18] H. L. Goering and W. D. Closson, *J. Amer. Chem. Soc.* **83**, 3511 (1961); Ref. 6, p. 390.

EXPERIMENTAL[19]

3-Bromocyclohexene[20] b.p. 55–58° (15 mm), n_D^{20} 1·5308 (lit. b.p. 55–57° (11 mm), n_D^{20}1·5308).

3-(*Δ^2-Cyclohexenyl)propene*-1. One-half mole of allyl magnesium bromide was prepared in 350 ml ether by dropwise addition under N over a period of 12 hr. The filtered soln was cooled in an ice-bath, and 53·7 g (0·33 mole) 3-bromocyclohexene dissolved in an equal volume of ether was added over a period of 7 hr under N. After standing overnight at room temp the product was washed, extracted, dried and distilled yielding 30·4 g. (0·249 mole) or 75% (based on 3-bromocyclohexene) of a colorless liquid, b.p. 147–149°, n_D^{20} 1·4722. The product appeared at least 98% pure by VPC analysis on a 10′ × ¼″ UCON LB 550X column at 150°. The IR spectrum showed vinyl absorption at 10·01 μ and 10·89 μ and *cis*-olefin absorptions at 13·87, 14·31 and 14·57 μ. The NMR showed an unresolved multiplet from 3·90 to 4·67 τ, a doublet at 4·94 τ, and a multiplet of at least 3 peaks at 5·15 τ. The integration showed olefinic and saturated protons in the ratio of 4·8:9·2.

3-(*Δ^2-Cyclohexenyl)propanol*-1. To 0·166 mole of bis-3-methyl-2-butylborane, freshly prepared in diglyme,[21] was added 18·3 g (0·150 mole) of 3-(Δ^2-cyclohexenyl)propene-1 at 0° over a period of 15 min. After the reaction had stood at 0° for 2·75 hr, excess hydride was decomposed by the careful addition of 20 ml water. The reaction mixture was cooled to 0°; 25 ml of 3N NaOH was added, and 25 ml 30% H_2O_2 was dropped in over 15 min. After 1 hr at room temp the layers were separated. Workup and distillation yielded 12·52 g (0·090 mole) of colorless liquid, b.p. 80–82° (8 mm), yield 59·7%. The IR spectrum showed absorption for an alcohol group and for a *cis*-ethylenic group. The NMR spectrum showed a triplet at 6·47 τ of the methylene protons adjacent to oxygen, a broad OH singlet at 5·11 τ, the olefinic singlet at 4·42 τ, and a totally unresolved aliphatic region.

3-(*Δ^2-Cyclohexenyl)propyl* p-*nitrobenzenesulfonate*. From 3·25 g (0·066 mole) of 3-(Δ^2-cyclohexenyl)-propanol-1 14·9 g of the corresponding *p*-nitrobenzenesulfonate (0·046 mole, 69·5%) was prepared by the usual procedure. After 6 recrystallizations from ether–pentane the pure white crystals melted at 61·5–62·5°. (Found: C, 55·24; H, 5·70; N, 4·12. Calc. for $C_{15}H_{19}NO_5S$: C, 55·37; H, 5·89; H, 4·31%).

The IR spectrum showed the absence of alcohol and the presence of *p*-nitrobenzenesulfonate (6·56 μ, 7·25 μ, 7·42 μ, 8·40 μ). The NMR spectrum was appropriately similar to that of the alcohol: quartet (4·1) at 1·80 τ, very broad singlet (1·9) at 4·52 τ, triplet (1·9) at 5·90 τ, unresolved multiplet (11·2) from 7·88 to 9·34 τ.

A sample of 3-(*Δ^2-cyclohexenyl)propyl acetate* (657 mg, 3·59 mmoles) was prepared from 3-(Δ^2-cyclohexenyl)propanol with Ac_2O in anhydrous pyridine. VPC analysis of the crude material on a 10′ diisodecyl phthalate column at 175° showed only 1 peak. IR: 5·74 (ester carbonyl), 6·06, 13·88, 14·30 and 14·78 μ.

3-*Cyclohexylpropyl* p-*nitrobenzenesulfonate* was prepared from 3-cyclohexylpropanol from the Aldrich Chemical Co. in 73·2% yield. After 3 recrystallizations from ether–pet. ether the white, crystalline solid melted at 80–81°. (Found: C, 55·16; H, 6·52; N, 4·43. Calc. for $C_{15}H_{21}NO_5S$: C, 55·02; H, 6·47; N, 4·28%).

3-*Cyclohexylpropyl acetate* yielded a single peak on VPC on a 10′ diisodecyl phthalate column at 175°. The IR spectrum indicated freedom from alcohol.

Solvolysis of 3-(*Δ^2-cyclohexenyl)propyl* p-*nitrobenzenesulfonate in acetic acid*. The sulfonate was heated at 100° for 18 hr (16 half-lives), 0·5003 g (1·54 mmole) being taken in 10 ml 0·2M AcONa in AcOH. The product was poured into 100 ml water, extracted 3 times with reagent grade pentane, the extracts washed with $NaHCO_3$ aq and NaCl aq and dried over $CaCl_2$. A calibrated amount of the standard (cyclohexylmethyl acetate) was added, and the soln was analyzed directly by VPC. (Samples of **36**, **34** and **39** were kindly supplied by Professor R. B. Woodward, as was a sample of the solvolysis product of the bicyclononyl tosylate in acetic acid.) The major components of this reaction product had been previously identified.[7] These samples were used with comparison of retention times and with peak enrichment on two columns to identify the products of solvolysis of **11**.

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[19] For more detail regarding the prep and solvolysis of 3-(Δ^2-cyclohexenyl)propyl *p*-nitrobenzenesulfonate and 3-cyclohexylpropyl *p*-nitrobenzenesulfonate, see the thesis of E. M. Nicholson, pp. 156–165, 174–178, and 215–230. Harvard University (1965).

[20] H. J. Dauben, Jr., and L. L. McCoy, *J. Amer. Chem. Soc.* **81**, 4863 (1959).

[21] H. C. Brown and G. Zweifel, *J. Amer. Chem. Soc.* **82**, 3222 (1960).

VPC analysis was carried out under two sets of conditions: (a) a 20′ × ⅛″ tris-β-cyanoethoxypropane on gas Chrom P column at 115°, and (b) a 10′ × ¼″ UCON LB 550X on Chromosorb P column at 175°. Standard solns of 3-(Δ^2-cyclohexenyl)propene-1, 3-(Δ^2-cyclohexenyl)propyl acetate, and cyclohexylmethyl acetate were used to determine area correction factors. The corrections, 1·03 and 1·08, were applied to all hydrocarbon products and all acetate products, respectively. On the TCEP column *cis–endo-*. hydrindyl acetate was not detectable because of overlap with 3-(Δ^2-cyclohexenyl)propyl acetate. On UCON the authentic sample was differentiated from the other products, but no trace of it was observed in the solvolysis product. Less than 0·5% could have been detected. Compound **34** forms merely a shoulder on the 3-(Δ^2-cyclohexenyl)propyl acetate peak on UCON. On TCEP **34** was clearly differentiated.

On UCON LB 550X at 125° the vapor chromatogram of the hydrocarbon products was similar to the chromatogram of the hydrocarbon products of bicyclononyl tosylate.[7] The two major peaks at 46·6 and 50·0 min were those identified by Foote and Woodward as *cis*-Δ^4-hexahydroindene and Δ^8-hexahydroindene (**39** and **42**) and were present in the ratio of 3·5 : 1 with **39** predominating.

After a similar product run buffered with urea instead of sodium acetate, the solvolysis product was distilled in a molecular still. The higher boiling portion which did not distil with the pot temp at 165° was reduced with LAH in ether. A product resulted which on Carbowax 20M (basic) at 150° showed two alcohols, 11·2% at 35·2 min and 89·8% at 50 min. These were collected and identified by their IR spectra as *cis–exo*-hydrindanol and 3-(Δ^2-cyclohexenyl)propanol, respectively. The VPC analysis of the collected 50-min peak on UCON showed a small amount of a second alcohol which was not identified but which was presumably 9-bicyclo(3.3.1)nonanol.

The acetolysis of *3-cyclohexylpropyl* p-*nitrobenzenesulfonate* carried out in similar fashion led to a product in 95% yield showing only one peak on VPC analysis with a diisodecyl phthalate column at 150°. The IR spectrum showed this product to be 3-cyclohexylpropyl acetate.

A mixture of cis- *and* trans-1,2-*cyclopentane diacetic acid* was prepared[22] from ethyl cyclopentylidenecyanoacetate-2-acetate[23] prepared from ethyl cyclopentanone-2-acetate.[22] The mixed stereoisomers of 1,2-cyclopentanediacetic acid, m.p. 167–168° (reported: *trans*, 132°; *cis*, 173°). A sample of the dimethyl ester, prepared with diazomethane, on a Carbowax VPC column showed a content of about 25% *trans* and 75% *cis*.

Diethyl 1,2-*cyclopentanediacetate* was prepared according to the procedures for ethyl adipate[24] was obtained in 98% yield as a colorless liquid, b.p. 113° (0·55 mm), 125° (1 mm), n^{25}_{D} 1·4496 (reported:[25] *cis*, b.p. 142–150° (5 mm) n^{25}_{D} 1·4518; *trans*, b.p. 99–118° (0·8–1·7 mm) n^{25}_{D} 1·4477).

Ethyl hydrogen 1,2-*cyclopentanediacetate* was prepared by stirring for 18 hr at 20–25° a soln of 100 g (0·413 mole) of the diethyl ester in 336 ml 1·23N ethanolic KOH and 540 ml EtOH; 15 g of the diethyl ester was recovered by extraction with ether after dilution with 200 ml water. Acidification, extraction, washing, and distillation yielded 58·4 g (66% yield) of the half-ester, b.p. 136–142° (0·15 mm). TLC analysis with 5% EtOH in AcOEt showed the product to be about 95% half-ester and 5% diacid.

1-(2-*Hydroxyethyl*)-2-(2-*dimethylaminoethyl*)*cyclopentane*. A soln of 56·0 g (0·262 mole) of the half-ester in 100 g $SOCl_2$ was stirred overnight at 20–25° and then at 75° for 15 min. The excess $SOCl_2$ was removed by distillation under red. press. and the last traces by codistillation with benzene. The crude acid chloride in 100 ml ether was then added dropwise to a stirred soln of 150 g dimethylamine in 300 ml ether cooled to −20°. The mixture was stirred at 20–25° for 3 hr and heated on a steam bath for 1 hr. The pptd amine hydrochloride was filtered and washed thoroughly with ether. The combined ether solns were dried over $MgSO_4$ and evaporated. The residue was distilled through a 6-in column packed with porcelain saddles to give 55·3 g (88% yield) of the ester-amide as a colorless liquid, b.p 118–120° (0·11 mm), n^{25}_{D} 1·4770–1·4785). The IR spectrum showed ester absorption at 5·8 μ and amide absorption at 6·1 μ.

The ester-amide was reduced with LAH.[26] The amino-alcohol was obtained in 92% yield as a colorless liquid, b.p. 83–85° (0·1 mm), n^{25}_{D} 1·4744–1·4760. (Found: C, 71·44; H, 12·67; N, 7·82. Calc. for $C_{11}H_{23}NO$: C, 71·29; H. 12·51; N, 7·56%).

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[22] R. P. Linstead and E. M. Meade, *J. Chem. Soc.* 935 (1934).

[23] S. Dev, *J. Ind. Chem. Soc.* **30**, 815 (1953).

[24] V. M. Micovic, *Org. Syn.* Col. Vol. **II**, 264 (1943).

[25] N. L. Allinger and V. B. Zalkow, *J. Amer. Chem. Soc.* **83**, 1144 (1961).

[26] V. M. Micovic and M. Lj. Mihailovic, *J. Org. Chem.* **18**, 1190 (1953).

2-(2-*Vinylcyclopentyl)ethanol* was prepared by the procedure for 1,2-divinylcyclopentane[27] by way of the amine oxide. Distillation of the product through a 6-in column packed with porcelain saddles gave 16·1 g (87% yield) of the unsaturated alcohol as a colorless liquid, b.p. 76–77° (1·4 mm), n_D^{25} 1·4752–1·4750. VPC on a Carbowax column at 140° showed 2 components, 20% *trans* isomer at retention time 7·5 min and 80% *cis* isomer at 10 min. (Found: C, 77·28; H, 11·62. Calc. for $C_9H_{16}O$: C, 77·10; H, 11·50%).

The *cis*- and *trans*-isomers were separated by preparative VPC on a Carbowax 20M column at 160°. The *trans*-isomer was collected from 53–62 min and the *cis*-isomer from 73–88 min.

cis-2-(2-*Vinylcyclopentyl)ethyl* p-*nitrobenzenesulfonate* (**13**) was prepared from the *cis*-alcohol and the *p*-nitrobenzenesulfonyl chloride.[28] The product from 1·30 g (93 mmole) of the *cis*-alcohol was 2·48 g (82% yield) after crystallization from ether–pentane at −20° of the ester as pale yellow plates, m.p. 51·5–52·5°. Recrystallization from ether–pentane raised the m.p. to 52–53°. (Found: C, 55·59; H, 5·90; N, 4·18; S, 9·65. Calc. for $C_{15}H_{19}NSO_5$: C, 55·36; H, 5·88; N, 4·31; S, 9·86%).

trans-2-(2-*Vinylcyclopentyl)ethyl* p-*nitrobenzenesulfonate* was obtained in 70% yield (0·742 g from 0·456 g of alcohol), m.p. 32–34·5°. Recrystallization from ether–pentane gave pale yellow plates, m.p. 32·5–34°. (Found: C, 55·32, H, 5·78; N, 4·00; S, 9·12%). Instability at room temp rendered this ester difficult to analyze.

cis-2-(2-*Vinylcyclopentyl)ethyl acetate* was prepared from the alcohol with Ac_2O and pyridine at room temp over a period of 2 days, n_D^{25} 1·4574. (Found: C, 72·32; H, 9·80. Calc. for $C_{11}H_{18}O_2$: C, 72·49; H, 9·95%).

trans-2-(2-*Vinylcyclopentyl)ethyl acetate*, n_D^{25} 1·4522. (Found: C, 72·74; H, 9·92%).

cis- *and* trans-1,2-*Divinylcyclopentanes* were prepared from the mixture of *cis*- and *trans*-1,2-cyclopentanediacetic acid.[27] The overall yield was 21% of a colorless liquid, b.p. 137–143°, n_D^{25} 1·4588 (reported:[27] *cis*, b.p. 140–141·5° (760 mm), n_D^{20} 1·4624; *trans*, b.p. 136–137·5° (760 mm), n_D^{20} 1·4552) VPC on an FFAP column at 85° showed the diolefin mixture to be composed of about 20% of the *trans*-isomer (ret. time 5 min) and about 80% of the *cis*-isomer (6·5 min). A preparative separation was achieved on an SE-30 column at 80° (*cis*, n_D^{25} 1·4604; *trans*, n_D^{25} 1·4530).

Hydrindene was prepared by the hydrogenation of indene at room temp over PtO_2,[29] yield: 92%, b.p. 79–80° (29 mm), n_D^{25} 1·5359 (reported: b.p. 79° (29 mm), $n_D^{20\cdot7}$ 1·5382).

Δ^8-Hexahydroindene was prepared by the reduction of hydrindene by Li in ethylamine.[30] From 10·0 g (0·085 mole) hydrindene was obtained 8·2 g of the olefin as a colorless liquid, b.p. 83° (69 mm), n_D^{25} 1·4864 (reported: b.p. 85° (50 mm), 96° (75 mm)).

cis-5-*Hydrindanol* was prepared by the hydrogenation of 5-indanol over PtO_2.[31] The alcohol product was obtained in a 57% yield as a colorless oil, b.p. 105° (10 mm), n_D^{25} 1·4952 (reported: b.p. 113° (15 mm), $n_D^{20\cdot5}$ 1·4913). The alcohol was homogeneous on a UCON column and on an FFAP column.

cis-Δ^4- *and* cis-*Δ^5-Hexahydroindene* were prepared in mixture by the $KHSO_4$ dehydration of *cis*-5-hydrindanol.[32,33] From 4·3 g (30·7 mm) of *cis*-5-hydrindanol there was obtained 3·0 g (80% yield) of the olefinic mixture, b.p. 103° (100 mm), n_D^{25} 1·4850 [reported: b.p. 165–170° (70 mm),[32] b.p. 100·5–103·5° (100 mm)[33]]. VPC on an FFAP column at 90° showed a major component (80%) at retention time 12·0 min and a minor component (20%) at 13·0 min.

The mixture was submitted to preparative VPC on a $AgNO_3$ column at 60°. The major component, *cis*-Δ^4-hexahydroindene, had an IR spectrum identical to that reported[7b] for the authentic material. Its NMR spectrum showed absorption for 2 olefinic protons as a multiplet at 5·55 ppm downfield from TMS. The minor component was identified as *cis*-Δ^5-hexahydroindene by its NMR spectrum which showed absorption by 2 olefinic protons as a triplet at 5·55 ppm and its IR spectrum which showed double bond absorption at 6·08 μ.

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[27] E. Vogel, K.-H. Ott and K. Gajek, *Liebigs Ann.* **644**, 172 (1961).

[28] A. Streitwieser and W. D. Schaeffer, *J. Amer. Chem. Soc.* **79**, 6236 (1957).

[29] M. A. Dolliver, T. L. Gresham, G. B. Kistiakowsky and W. E. Vaughan, *J. Amer. Chem. Soc.* **59**, 83 (1937).

[30] P. E. Fuchs, Ph.D. Thesis, p. 85. Harvard University (1956).

[31] A. H. Cook and R. P. Linstead, *J. Chem. Soc.* 946 (1934).

[32] W. Hückel and E. Goth, *Ber. Dtsch. Chem. Ges.* **67**, 2104 (1934).

[33] K. Alder and H. A. Dortmann, *Chem. Ber.* **87**, 1905 (1954).

cis-endo-*Hydrindan-4-ol* was prepared[34] by the hydrogenation of 8·1 g (60·4 mmole) of 4-indanol (Aldrich Chemical Co.) in 40 ml water over 270 mg Pt black and 1·0 g platinic acid at room temp and 2–3 atm press. Workup and distillation through a short column gave 5·1 g (60% yield) of a colorless, viscous oil, b.p. 115–117° (17 mm), n_D^{26} 1·4978 [reported: b.p. 107–109° (15 mm)]. The alcohol was homogeneous on an FFAP column and had an IR spectrum identical to one reported for the authentic material.[7b]

$\Delta^{4(8)}$-*Hexahydroindene*. A mixture of 0·88 g (6·3 moles) of *cis-endo*-hydrindan-4-ol and 0·15 g $KHSO_4$ was heated in a flask attached to a short distillation column at 170–185° (160 mm). The distillate, b.p. 70–130°, was diluted with pentane, dried over neutral alumina and evaporated. The residue (0·7 g) was submitted to preparative VPC on a $AgNO_3$ column. The first component collected (about 20% of the mixture) was identified as $\Delta^{4(8)}$-hexahydroindene by its NMR spectrum which showed absorption for 1 olefinic proton at 5·1 ppm. The second fraction, about 10%, was not collected in pure form. However, VPC retention time comparisons identified it as *cis*-Δ^4-hexahydroindene. The third component, about 70%, was identified as Δ^8-hexahydroindene by retention time and IR spectral comparison with an authentic sample.

Products of the acetolysis of cis-2-(2-*vinylcyclopentyl*)*ethyl* p-*nitrobenzenesulfonate* (**13**). A soln of 0·325 g (1·0 mmole) of **13** and 0·164 g (2·0 mmole) NaOAc in 10 ml anhyd AcOH was heated under an atm N at 75·5° for 24 hr (6 half-lives). The soln was cooled, diluted with 20 ml water, and extracted with pentane. The pentane extracts were washed with sat $NaHCO_3$ aq, dried over Na_2SO_4, and concentrated to exactly 5 ml through an efficient 20-cm vacuum-jacketed Podbielniak Heli-Pak column. To a 1·0-ml aliquot of this product soln was added 1 ml of a standard (0·031 M) soln of cyclohexylacetate in pentane. The hydrocarbon products were identified by retention time comparisons with authentic samples of *cis*-Δ^4-, *cis*-Δ^5-, Δ^8-, and $\Delta^{4(8)}$-hexahydroindene on FFAP, Apiezon N, and Silicone 710 columns. The retention times observed for these standards are tabulated in Table 7. The relative peak areas for the hydrocarbons and the cyclohexyl acetate were 1·76 to 1·0, respectively. These values were then corrected by the area factor ($f = 1{\cdot}27$) which was obtained from standard solns of Δ^8-hexahydroindene and cyclohexyl acetate. The detector responses of the other hydrocarbon components were assumed to be identical with that of Δ^8-hexahydroindene.

The acetate products were analyzed by retention time comparisons with authentic samples of *cis*-2-(2-vinylcyclopentyl)ethyl acetate and of **35**, **36** and **37** on three different VPC columns. See Table 7. Samples of the latter three acetates were obtained from the acetolysis of **14**.[7] *cis*-5-Hydrindyl acetate (**38**) of unknown configuration could not be separated from **36** on the VPC columns used. However, after LAH reduction of the acetolysis product, *cis*-5-hydrindanol was identified in the VPC by retention time comparison with authentic material, also of unknown configuration. (See above.) The cyclohexyl acetate was used in these VPC analyses again as a standard. Standard solutions of *cis*-2-(2-vinylcyclopentyl)ethyl acetate and cyclohexyl acetate gave the area factor ($f = 1{\cdot}33$), and this factor was used for the other product acetates.

Another experiment was carried out on a 1·5 g scale, and the acetolysis mixture was submitted to preparative VPC. The acetates **35** and **36** were collected in nearly pure form on a UCON column. After LAH reduction the corresponding alcohols had IR spectra identical with those reported for the authentic samples.[7] From the UCON column *cis*-2-(2-vinylcyclopentyl)ethyl acetate and equatorial *trans*-hydrindyl acetate (**37**) were collected as a mixture. After LAH reduction the corresponding 2 alcohols were separated on a TCEP column. The IR spectrum of the equatorial *trans*-4- hydrindanol had bands at 9·09, 9·44, 9·68 and 9·84 μ as reported for the authentic material.[7b] From preparative VPC on an SE-30 column a sample of *cis*-Δ^4-hexahydroindene (**39**) was collected in pure form and had an IR spectrum identical with that of an authentic sample. A sample of Δ^8-hexahydroindene (**42**) was also collected; its IR spectrum showed absorptions for all the bands present in the spectrum of the authentic material and, in addition, a small absorption at 6·08 μ, apparently due to a small amount of *cis*-Δ^5-hexahydroindene.

Acetolysis of trans-2-(2-*vinylcyclopentyl*)*ethyl* p-*nitrobenzenesulfonate* (**12**). A soln of 0·325 g (1·0 mmole) of **12** and 0·164 g (2·0 mmoles) of NaOAc in 10 ml anhydr AcOH was heated under an atm N at 94° for 24 hr. The soln was cooled, diluted with 20 ml water, and extracted with pentane. Washing, drying and VPC analysis as above showed the acetolysis products to be acetates, except for a trace amount of *trans*-1,2-divinylcyclopentane. The acetate products were identified as 95%

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[34] W. Hückel, E. Goth and G. Demmler, *Ber. Dtsch. Chem. Ges.* **67**, 2102 (1934).

TABLE 7. CALIBRATION OF GAS CHROMATOGRAPHIC COLUMNS

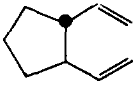
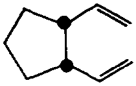
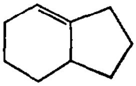
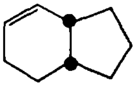
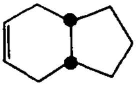
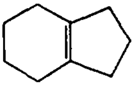
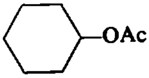
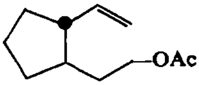
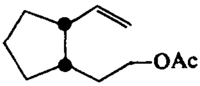
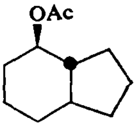
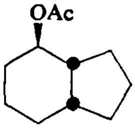
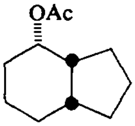
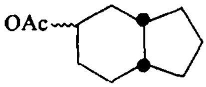
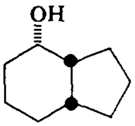
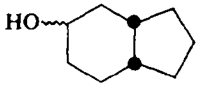
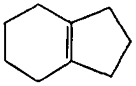
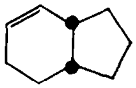
Sample	FFAP	Retention time (min)			
		(114°) Apiezon N	(135°) Silicone 710	(134°) UCON	(121°) Carbowax
	4·2 (90°)				
	5·0 (90°)				
	10·5 (90°)	23·0	10·5		
	12·0 (90°)	25·5	12·0		
	18·2 (75°)^a		36·0 (103°)^b		
	13·0 (90°)	27·5	13·0		
	6·0 (134°)				
	30·0 (134°)			22·0	12·0
	35·5 (134°)			23·5	16·0
	34·0 (134°)			24·0	13·5

TABLE 7—*continued*

Sample	FFAP	Retention time (min)			
		(114°) Apiezon N	(135°) Silicone 710	(134°) UCON	(121°) Carbowax
	37·0 (134°)			26·0	16·0
	43·0 (134°)			30·0	18·0
	~43·0 (134°)			~30·0	~18·0
	18·0 (165°)			14·0 (150°)	
	20·0 (165°)			15·0 (150°)	

[a] Not resolved from  at 90°.

[b] Not resolved from  at 135°.

trans-2-(2-vinylcyclopentyl)ethyl acetate and 5% *trans*-equatorial-4-hydrindyl acetate by retention time comparisons with authentic samples on the FFAP, UCON and Carbowax columns. See Table 7.

Vapor phase chromatography. The VPC analyses were performed on Aerograph Hi-Fi VPC apparatus Models A-600B and A-325 equipped with a H flame ionization detector. N was used as a carrier gas at a flow rate of approximately 25 ml/min. Relative peak areas were determined with a disc chart integrator. Analyses were carried out on a 6′ × ⅛″ column packed with 20% free fatty acid polymer ("FFAP") on DMCS Chromosorb W, a 10′ × ⅛″ column packed with 30% silicone 710, a 5′ × ⅛″ column packed with Apiezon N on 60/80 Chromosorb P, a 5′ × ⅛″ column packed with 10% Carbowax 1500 on 45/60 Chromosorb P, a 6′ × ⅛″ column packed with 10% UCON on 60/80 Diatoport W. Preparative VPC separations were performed on Aerograph VPC apparatus Model A 700 with He as carrier gas. A 19′ × ⅜″ column packed with 20% Carbowax 20M on Chromosorb P, a 20′ × ⅜″ column packed with 35% $AgNO_3$ on diethylene glycol, a 19′ × ⅜″ column packed with 20% UCON on

Chromosorb P, a 20′×⅜″ column packed with 30% SE-30 on Chromosorb P, or a 20′×⅜″column packed with 20% TCEP on Chromosorb P were used.

In all quantitative determinations standard solns of cyclohexyl acetate, cyclohexylmethyl acetate, *cis*-2-(2-vinylcyclopentyl)ethyl acetate, or Δ^8-hexahydroindene in ether or pentane were used to calibrate the chromatogram for specific areas.

Rate measurements. The rate determinations of compound **11** were all carried out by the standard titrimetric method using sealed ampoules and samples being titrated in AcOH to the bromphenol blue end point. The data were tested visually for internal consistency by making plots of the quantity $\log[(v_\infty - v_t)/(v_\infty - v_0)]$ against time. The rate constants and activation parameters were determined on an IBM 1620 computer using programs provided by J. M. McBride and J. M. Wright, respectively. The calculated and observed infinity titers usually agreed within 2%, and the plots were linear over several half-lives. The titrimetric technique is suitable for determining rate constants in the presence or absence of excess AcONa.

The acetolysis of the esters **12** and **13** in 0·03 M AcONa was followed by the conductimetric technique.[2a] A linear relationship between conductance and concentration for solns of *p*-nitrobenzenesulfonic acid between 0·002 and 0·03 M in 0·03 M AcONa in AcOH was verified empirically. Rate constants were determined from the plot of $1/r_\infty - 1/r_t$ against time on semilogarithmic paper. The activation parameters were determined and interpolations were performed using a computer program. The conductimetric method is not well adapted to determining rates of reaction in the absence of excess sodium acetate.

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