

spectrum at $-80\text{ }^{\circ}\text{C}$ for the undeuterated methine and methylene at $\delta(^{13}\text{C})$ 4.93 and 17.60 (Figure 1) is almost identical with those of the symmetrical all-proton ion **9** ($\delta(^{13}\text{C})$ 4.90 and 17.60).¹³ The deuterated methine triplet ($J_{\text{C-D}} = 24.9\text{ Hz}$) was found less than 0.2 ppm shielded from the undeuterated methine peak, indicating only an isotopic perturbation of resonance. These observations fully support the symmetrical nonclassical structure of **9**. Similar results have been obtained by Saunders and co-workers³ previously on the related Coates's cation¹⁸ (i.e., the trishomocyclopropenyl-9-pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonyl cation) by deuterium substitution at the C₉ position.

Conclusion

The application of Saunderson's isotopic perturbation method of equilibria to 1-methylcyclobutyl cation **1** and trishomocyclo-

propenyl cation **9** supports their σ -bridged nonclassical structures.

Experimental Section

The α,α -dideuterio-1-methylcyclopropylcarbinol and *cis*-3-deuterio-bicyclo[3.1.0]hexan-3-ol were prepared by LiAlD_4 reduction of 1-methylcyclopropanecarboxylic acid (purchased from Aldrich) and bicyclo[3.1.0]hexan-3-one¹⁹ in diethyl ether.

Preparation of Ions. Freshly double-distilled SbF_5 was used. To SbF_5 dissolved in about fourfold excess of SO_2ClF at dry ice/acetone temperature ($-78\text{ }^{\circ}\text{C}$) was added with vigorous stirring a cooled slurry or solution of the appropriate precursor in SO_2ClF so as to obtain approximately 10–15% solution of the ion.

¹³C NMR spectra were obtained with Varian Model XL-200 NMR spectrometer equipped with a low-temperature broad-band probe. Chemical shifts are referenced from capillary tetramethylsilane.

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Enthalpies of Hydration of Alkenes. 3. Cycloalkenes

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Abstract: The enthalpies of reaction of cyclopentene, cyclohexene, 1-methylcyclopentene, methylenecyclopentane, 1-methylcyclohexene, methylenecyclohexane, bicyclo[2.2.1]hept-2-ene, and bicyclo[2.1.1]hex-2-ene with trifluoroacetic acid were measured. This gives the difference in energy between exo- and endocyclic double bonds with very good precision and gives differences in driving force for addition reactions in the bicyclic systems. In the series cyclopentene, bicycloheptene, and bicyclohexene, the enthalpies of reaction with trifluoroacetic acid are 9, 15, and 23 kcal/mol, respectively. The enthalpies of conversion of the corresponding alcohols to the trifluoroacetates also were measured, allowing the enthalpies of formation of the alcohols to be determined. It is found that the enthalpy change for replacing a hydroxy group by methyl is essentially constant for a given type of alcohol (i.e., primary, secondary, or tertiary), but it varies considerably between groups.

We have developed a procedure whereby the enthalpies of hydration of alkenes may be measured experimentally.¹ It involves the reactions of the alkene and of the product alcohol with trifluoroacetic acid containing trifluoroacetic anhydride, leading in both cases to the same trifluoroacetate products. The difference in enthalpies of reaction along with the enthalpy of reaction of water allows the calculation of the enthalpy of hydration.

The data may be used to determine the relative energies of related alkenes, as well as the enthalpies of formation of the product alcohols. The procedure possesses the generality associated with enthalpies of hydrogenation of alkenes² but provides data of higher precision and leads to an alcohol as the product rather than the nonfunctionalized alkane. When the enthalpies of formation of the alkenes are known, the method allows the enthalpies of formation of the alcohols to be determined. This is of particular value since there is a relative lack of such information for alcohols.

We have applied the procedure to the study of the series of C₅, C₆, and C₇ *n*-alkenes.^{1,3} It was possible to show that some of the earlier combustion data for the hexenes were significantly in error and to revise the ΔH_f . Enthalpies of formation of the 2-, 3-, and 4-heptanols and 3-hexanol were obtained.

We now report the continuation of this study using a series of cyclic alkenes which are of greater chemical interest than the *n*-alkenes. The compounds include cyclopentene (**1**), cyclohexene

Table I. Enthalpies of Trifluoroacetolysis of Alkenes

compound	state	<i>n</i> ^a	ΔH_r , ^b cal/mol
cyclopentene (1)	<i>l</i>	3	-9167 ± 44
cyclohexene (2)	<i>l</i>	4	-10355 ± 25
<i>cis</i> -3-hexene	<i>l</i>		-10514 ± 29^c
1-methylcyclopentene (3)	<i>l</i>	3	-7250 ± 3
methylenecyclopentene (4)	<i>l</i>	3	-10900 ± 21
1-methylcyclohexene (5)	<i>l</i>	4	-8739 ± 21
methylenecyclohexane (6)	<i>l</i>	4	-10710 ± 24
bicyclo[2.2.1]hept-2-ene (7)	<i>c</i>	10	-14575 ± 54
	<i>l</i>		-15333 ± 55
bicyclo[2.1.1]hex-2-ene (8)	<i>l</i>	3	-23757 ± 117

^a Number of runs. ^b Uncertainties are twice the standard deviation of the mean (2 σ). ^c Reference 1. The value corresponds to the formation of the 3-trifluoroacetate as the product.

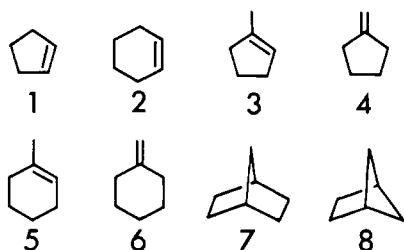
Table II. Enthalpies of Fusion

compound	<i>n</i> ^a	ΔH (cal/mol)
1-methylcyclopentanol	3	2011 ± 4
1-methylcyclohexanol	3	2599 ± 7
<i>exo</i> -bicyclo[2.2.1]heptan-2-ol	3	621 ± 11
bicyclo[2.1.1]hexan-2-ol	3	545 ± 6
bicyclo[2.2.1]hept-2-ene	3	758 ± 8

^a Number of runs.

(**2**), 1-methylcyclopentene (**3**), methylenecyclopentane (**4**), 1-methylcyclohexene (**5**), methylenecyclohexane (**6**), bicyclo[2.2.1]hept-2-ene (norbornene, **7**), and bicyclo[2.1.1]hex-2-ene (**8**). The reactions of **1** and **2** with trifluoroacetic acid proceeded

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slowly and required acid catalysis in order to achieve a suitable rate. They were studied in a medium containing 0.002 M trifluoromethanesulfonic acid and 0.25 M trifluoroacetic anhydride in trifluoroacetic acid. The other six alkenes, 3–8, were more reactive and did not require acid catalysis. The enthalpies of reaction are given in Table I. In order to be able to make comparisons with all compounds in the same phase, the enthalpy of fusion of norbornene was determined via differential scanning calorimetry, giving the value listed in Table II.

The enthalpies of trifluoroacetylolysis of cyclohexene and *cis*-3-hexene¹ are rather similar ($\Delta\Delta H = 160$ cal/mol), as might be expected from the similarity of their structures. The trifluoroacetylolysis of cyclopentene is considerably less exothermic than that of cyclohexene and is a reflection of the increase in torsional strain for cyclopentene when the two sp^2 centers are converted into sp^3 .⁴ The reactions of the alkenes 3–6 which lead to tertiary trifluoroacetates probably give equilibrium mixtures of the trifluoroacetates and alkenes,⁵ and thus a comparison of the enthalpies of reaction of 1 and 3 with trifluoroacetic acid is not meaningful. However, 3 and 4 as well as 1-methylcyclopentanol will all lead to the same product mixture and so a comparison of their enthalpies of reaction is useful. The same is true with 5, 6, and 1-methylcyclohexanol.

Since 3 and 4 give the same product, the difference in enthalpy of reaction directly gives the difference in enthalpy of formation. The same is true with 5 and 6. The values for a series of ring sizes are compared in Table III. Information on these reactions has been available from enthalpies of combustion and of hydrogenation. The combustion experiments unavoidably have relatively large uncertainties (generally 300–600 cal/mol), leading to even larger uncertainties in the enthalpies of isomerization. Reaction calorimetry generally provides higher precision, and there is reasonable agreement between the present data and the enthalpies of hydrogenation determined by Turner et al.⁶ The values, however, are not directly comparable since the hydrogenation experiments were carried out with the reactants in acetic acid solution whereas our data refer to the pure liquid state. The two sets of enthalpies of isomerization thus differ by the unknown differential enthalpies of solution of the two alkenes being compared. In any event, the results again demonstrate the high precision which may be achieved in determining the enthalpy difference between pairs of isomeric alkenes. It would be desirable to report the ΔH values for the gas phase since this would eliminate intermolecular interactions. However, the needed enthalpies of vaporization are presently not known.

The reversal in the sign of ΔH for the cyclopropyl case in comparison to the other ring systems is of course related to the difficulty in introducing a trigonal center into a three-membered ring (13 kcal/mol destabilization per trigonal center⁷), and a similar but much smaller destabilization is found with a cyclobutane ring (1 kcal/mol per trigonal center⁷) leading to a small enthalpy of isomerization. The ΔH found for the conversion of 6 to 5 (1.97 ± 0.03 kcal/mol) is close to that reported for the

Table III. Enthalpies of Isomerization

reaction	ΔH		
	hydration	hydrogenation	combustion
			$+10290 \pm 520^a$
		-950 ± 61^b	
	-3650 ± 22^c	-3870 ± 45^b	-3860 ± 270^c
	-1971 ± 32^c	-2340 ± 170^b	-4700 ± 920^c

^a Gas-phase values.⁷ ^b All components in acetic acid solution.⁶
^c Liquid-phase values.

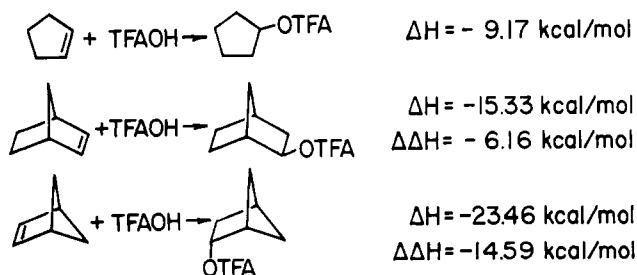
Table IV. Enthalpies of Reaction of Alcohols with Trifluoroacetic Anhydride

compound	state	<i>n</i>	ΔH_r (cal/mol)
cyclopentanol	<i>l</i>	5	-22219 ± 56
cyclohexanol	<i>l</i>	4	-21524 ± 37
1-methylcyclopentanol	<i>c</i>	6	-18116 ± 30
	<i>l</i>		-20127 ± 30
1-methylcyclohexanol	<i>c</i>	4	-20796 ± 21
	<i>l</i>		-23395 ± 22
<i>exo</i> -bicyclo[2.2.1]heptan-2-ol	<i>c</i>	5	-21013 ± 32
	<i>l</i>		-21771 ± 34
bicyclo[2.1.1]hexan-2-ol	<i>c</i>	5	-21308 ± 54
	<i>l</i>		-21853 ± 54

conversion of 2-methyl-1-butene to 2-methyl-2-butene (-1.86 ± 0.25 kcal/mol)⁸ and may be considered to be a normal value. The larger enthalpy of isomerization of methylenecyclopentane is a result of having four partially eclipsed methylene groups whereas 1-methylcyclopentane has only three.

The enthalpy of formation of 1-methylcyclohexene is reasonably well known⁹ (-19.40 ± 0.19 kcal/mol, liquid). The present data then allow the calculation of a much improved enthalpy of formation of methylenecyclohexene (-17.43 ± 0.20 , liquid) vs. -14.7 ± 0.9 .¹⁰

The reactivity of bicyclic alkenes such as norbornene and bicyclo[2.1.1]hex-2-ene has been of interest,^{11–14} and it has been concluded that the high reactivity of norbornene results from the enforced staggering of allylic bonds in this alkene.¹⁴ Here, it is important to have information of the thermochemical driving force available to facilitate reactions. A comparison of cyclopentene, norbornene, and bicyclohexene is shown below: In each case,



a double bond in a five-membered ring is converted to a tri-

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Table V. Enthalpies of Hydration of Alkenes (cal/mol)

compound	ΔH_f
cyclopentene (1)	-5000 \pm 71
cyclohexene (2)	-6731 \pm 38
cis-3-hexene	-6360 \pm 81 ^a
1-methylcyclopentene (3)	-5130 \pm 43
methylenecyclopentane (4)	-8780 \pm 47
1-methylcyclohexene (5)	-3351 \pm 43
methylenecyclohexene (6)	-5322 \pm 44
bicyclo[2.2.1]hept-2-ene (7)	-11569 \pm 71
bicyclo[2.1.1]hex-2-ene (8)	-19911 \pm 132

^a Reference 1. The value corresponds to the formation of 3-hexanol.**Table VI.** Enthalpies of Solution of Trifluoroacetates

compound	<i>n</i>	[H ⁺] (M)	ΔH_{soln} (cal/mol)
cyclopentyl	4	0.002	-911 \pm 20
	2	0.000	-971 \pm 1
cyclohexyl	3	0.002	-1077 \pm 15
	3	0.000	-985 \pm 17
trifluoroacetic acid	1	0.002	-2
	1	0.000	-17

fluoroacetate, and thus a direct comparison is appropriate. It can be seen that norbornene has over 6 kcal/mol additional driving force for addition to the double bond and that bicyclohexene has 14.6 kcal/mol extra driving force. The latter is considerably larger than that which had been estimated via molecular mechanics.⁸ The similarity in cycloaddition rates for norbornene and bicyclohexene, despite the large difference in enthalpies of reaction, strengthens the view that the high reactivity of norbornene is not largely derived from strain relief and that there is a specific structural factor operating in this case.¹²⁻¹⁴ One may, however, wonder if any one of the current hypotheses is adequate to explain the observations in view of the large difference in enthalpies of reaction.

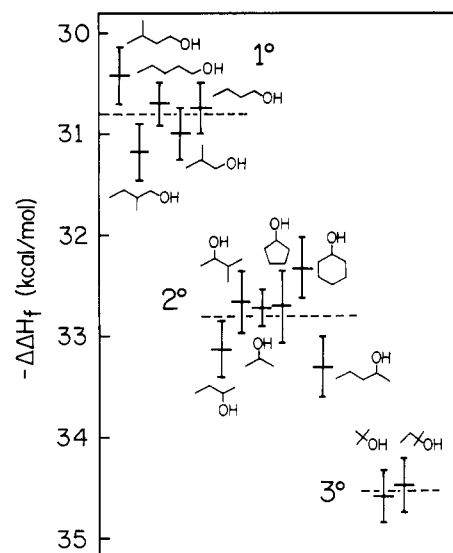
The second half of this study involved the measurement of the enthalpies of reaction of the alcohols corresponding to the trifluoroacetates with trifluoroacetic anhydride in trifluoroacetic acid. In the case of norbornene, it is known that the addition of trifluoroacetic acid gives 98.98% *exo*-trifluoroacetate.¹⁵ The enthalpies of reaction are given in Table IV. Using the enthalpy of reaction of water with trifluoroacetic anhydride in trifluoroacetic acid (-18007 \pm 30 cal/mol) the enthalpies of hydration of the alkenes now could be calculated, giving the values summarized in Table V. For comparison, the previously reported value for 3-hexene going to 3-hexenol¹ also is given.

The use of these data presents two problems. All of the tertiary alcohols, 9-12, were solids, whereas cyclopentanol (7) and cyclohexanol (8) were liquid. In order to be able to compare the reactions, it is necessary to have data for all compounds in the pure liquid phase. Therefore, the enthalpies of fusion were determined by differential scanning calorimetry, giving the values summarized in Table II. The enthalpies of hydration in Table V all refer to the conversion of liquid alkenes to liquid alcohols. In the cases of cyclopentene and cyclohexene, an acid catalyst was required in order to achieve a rapid reaction. It was then necessary to correct for the difference in enthalpy of solution of the product trifluoroacetates in media with and without the strong acid. The required data are given in Table VI.

It is now possible to obtain enthalpies of formation of the alcohols based on the enthalpies of hydration, the reported enthalpies of formation of the alkenes, and the enthalpy of formation of water (-68.315 kcal/mol).⁸ The values are given in Table VII and where possible are compared with the literature values. The enthalpies of formation appear to be well established for cyclopentene and cyclohexene, and the values for 1-methylcyclopentene and 1-methylcyclohexene appear to be quite reasonable.⁸ There

Table VII. Enthalpies of Formation of Alcohols (kcal/mol)

compound	state	ΔH_f	
		this work	literature ^g
cyclopentanol	<i>l</i>	-71.80 \pm 0.25 ^a	-71.71 \pm 0.30
cyclohexanol	<i>l</i>	-84.13 \pm 0.16 ^b	-83.20 \pm 0.40
1-methylcyclopentanol	<i>l</i>	-82.11 \pm 0.18 ^c	-82.3 \pm 0.6
	<i>c</i>	-84.12 \pm 0.18	
1-methylcyclohexanol	<i>l</i>	-91.07 \pm 0.20 ^d	
	<i>c</i>	-93.67 \pm 0.20	
<i>exo</i> -bicyclo[2.2.1]heptan-2-ol	<i>l</i>	-66.62 \pm 0.50 ^e	
	<i>c</i>	-67.24 \pm 0.50	
bicyclo[2.1.1]hexan-2-ol	<i>l</i>	-38 \pm 3 ^f	
	<i>c</i>	-38 \pm 3	

^a Based on ΔH_f for cyclopentene, +1.52 \pm 0.24 kcal/mol (1).⁸^b Based on ΔH_f for cyclohexene, -9.08 \pm 0.15 kcal/mol (1).⁸^c Based on ΔH_f for 1-methylcyclopentene, -8.66 \pm 0.17 kcal/mol (1).⁸^d Based on ΔH_f for 1-methylcyclohexene, -19.40 \pm 0.19 kcal/mol (1).⁸^e Based on ΔH_f for bicyclo[2.2.1]hept-2-ene, 13.20 \pm 0.50 kcal/mol (1).^{17,18}^f Based on estimate ΔH_f for bicyclo[2.1.1]hex-2-ene, 50 \pm 3 kcal/mol (1), see text. ^g Reference 8.**Figure 1.** Enthalpy changes for the replacement of a hydroxy group by a methyl group.

has been some controversy concerning the enthalpy of formation of bicyclo[2.2.1]hept-2-ene,¹⁶ and we have used the average of the recent values derived from the enthalpy of combustion¹⁷ and from equilibrium measurements.¹⁸ No experimental value is available for bicyclo[2.1.1]hex-2-ene, but an estimate of ΔH_f = 57 \pm 3 kcal/mol (g) has been derived via an extended basis set (6-31G*) ab initio calculation.¹⁹ With use of an estimated ΔH_f = 7.2 kcal/mol (see Experimental Section), the liquid-phase ΔH_f was taken as 50 \pm 3 kcal/mol.

The present ΔH_f for cyclopentanol is in good agreement with the literature value, but in the case of cyclohexanol, the new ΔH_f is almost 1 kcal/mol more negative than the "selected value".⁸ There are three values in the literature which are not in good agreement. We shall show below that the present value is in better agreement with a simple correlation than are the older values. The only other alcohol in our series which has been studied is 1-methylcyclopentanol, and the reported ΔH_f is in good agreement with the present value.

A methyl group has a size similar to that of a hydroxy group, and one might expect that intramolecular interactions would be similar for the two groups in the absence of hydrogen bonding (i.e., in the gas phase). Then, for a given type of alcohol (primary, secondary or tertiary), one would expect to find a relatively

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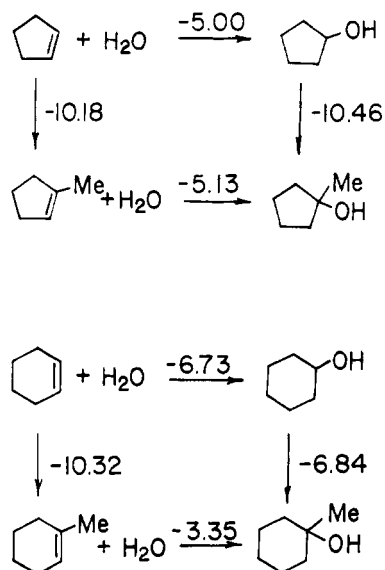


Figure 2. Enthalpy changes for hydration and for the replacement of hydrogens by methyl groups. The energies are in kcal/mol.

constant change in ΔH_f for the replacement of a methyl group by hydroxy. A test of this hypothesis is shown in Figure 1.

It can be seen that the data fall into three rather tight groups, with relatively large differences between the primary, secondary, and tertiary cases. The point for cyclohexanol is that obtained in this investigation. The previously reported value would have led to an energy difference ~ 1 kcal/mol smaller than that for the other secondary alcohols, which is quite unreasonable. The energy differences are 30.80 ± 0.26 for the primary alcohols, 32.80 ± 0.32 for the secondary alcohols, and 34.53 for the tertiary alcohols. In the case of the primary alcohols, there is a suggestion of a smaller difference (~ 0.5 kcal/mol) between those with and without a branch at the β carbon. However, this difference appears to be too small to be statistically significant.

The energy differences may well contain a small contribution from a difference in steric interactions between a methyl and a hydroxy group as the substituent. We plan to test this by examining cases in which such a steric effect should be more important than in the present group of compounds. Nevertheless, it seems likely that some of the differences represent an electronic effect. The hydroxy group is electron withdrawing with respect to an sp^3 -hybridized carbon, and part of the energy differences between types of alcohols may reflect the stabilization of the electron deficient α carbon by the alkyl groups.

We may now examine how ring size and alkyl substitution affect the enthalpies of hydration. The energy changes for group substitution in the cyclopentane and cyclohexane series are compared in Figure 2. It can be seen that the substitution of a methyl for a vinyl hydrogen in the alkenes produces essentially the same energy change, which is about the same as the energy change for replacing the α proton of cyclopentanol with a methyl. The smaller hydration enthalpy for cyclopentene again reflects the increase in torsional strain in going to cyclopentanol. The only compound of the group which appears to be out of line is 1-methylcyclohexanol. This is destabilized by the necessity of one of the groups occupying an axial position, and possibly also by the steric effect associated with the smaller $\text{H}_3\text{C}-\text{C}-\text{O}$ angle in cyclohexane than in cyclopentane. The same effect may be seen in the replacement of the tertiary hydrogen of the 1-methylcycloalkanes by methyl where the energy change is 6.0 kcal/mol with the C_5 ring and 4.0 kcal/mol for the C_6 ring.⁸

The question of the origin of the energy changes in these and some related systems could be better examined if the energy changes could be compared in the gas phase rather than in the liquid phase. This requires experimental data on the enthalpies

of vaporization. We have constructed an automated vaporization calorimeter based on the calorimetric design of Wadso²⁰ and have begun a systematic study of the enthalpies of vaporization of these and related compounds. The data will be presented at a later time.

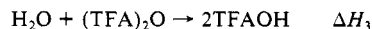
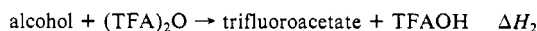
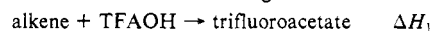
Experimental Section

Materials. Cyclopentene, cyclohexene, 1-methylcyclopentene, 1-methylcyclohexene, and methylenecyclohexene were 99+% commercial samples. They were distilled before use, collecting a center fraction. Analysis by GC showed no observable impurities. Commercially available methylenecyclopentane contained considerable 1-methylcyclopentene. It was prepared by a Wittig reaction starting with cyclopentanone²¹ and was purified by preparative GC. Norbornene was a commercial sample and was distilled from calcium hydride. Analysis of GC and NMR indicated no significant impurities. Bicyclo[2.1.1]hex-2-ene was prepared by the literature procedure.²² It was purified by preparative GC with an XF-1150 column.

Cyclopentanol, cyclohexanol, 1-methylcyclopentanol, 1-methylcyclohexanol, and *exo*-norbornanol were commercial samples. The first two alcohols were purified by heating with calcium hydride overnight, followed by distillation through a 25 cm vacuum jacketed glass helix filled column. The samples were protected from moisture at all times. 1-Methylcyclopentanol and bicyclo[2.1.1]hexan-2-ol were dissolved in a minimum amount of ether and were purified by gas chromatography with a DC-200 column. 1-Methylcyclohexanol and *exo*-norbornanol were distilled from calcium hydride, taking a large fore-run.

The solvent, 0.25 M trifluoroacetic anhydride in trifluoroacetic acid, was prepared as previously described.¹

Calorimetry. The calorimetric studies were carried out by using a modified version of the automated calorimeter previously described.²³ It was checked by using the reaction of Tris (NBS standard reference material 724a) with 0.1 N hydrochloric acid. The average value for 26 runs carried out over a 3-month period was -7117 ± 5 cal/mol. The recommended value is -7116 ± 8 cal/mol.²⁴ The alkenes 3-8 reacted with the reaction solvent at a rapid rate in the absence of an acid catalyst. Similarly, the corresponding alcohols reacted rapidly with the solvent to form the same products. The enthalpy of reaction of water was previously determined to be -18007 ± 30 cal/mol. The enthalpies of hydration were calculated from the following reactions:



$$\Delta H_r = \Delta H_1 - \Delta H_2 + \Delta H_3$$

cyclopentene and cyclohexene, it was necessary to make the reaction solution 0.002 M in trifluoromethanesulfonic acid in order to achieve a rapid reaction. However, cyclopentanol and cyclohexanol reacted only slowly in the presence of the strong acid, probably being converted to the oxonium ion. Therefore, it was necessary to correct for the difference in enthalpy of solution of the trifluoroacetates with and without the strong acid. The correction was small and is given by the data in Table VI.

The heats of fusion were determined on a Perkin Elmer DSC-4 differential scanning calorimeter with System 4 Microcomputer Controller and Thermal Analysis Data Station. It was calibrated with indium, and benzoic acid was used as a secondary standard. Three sample pans for each compound were prepared, and at least two runs were made on each pan.

The estimation of the heat of vaporization of bicyclo[2.1.1]hex-2-ene made use of the observation that a plot of ΔH_v vs. boiling point is linear for compounds with a given functional group.²⁵ A plot of this type for seven cyclic olefins yielded a good straight line with slope 0.0398 and intercept -6.039 ; the root mean square error was 121 cal. For the bicyclic olefin with boiling point 60 °C, the estimated ΔH_v is 7.21 kcal/mol.

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Registry No. 1, 142-29-0; 2, 110-83-8; 3, 693-89-0; 4, 1528-30-9; 5, 591-49-1; 6, 1192-37-6; 7, 498-66-8; 8, 822-41-3; trifluoroacetic anhydride, 407-25-0.

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