All carbonyl compounds, with the exception of **3**, were commercial products and were distilled prior to use. In general, the photochemistry of these molecules is not very sensitive to impurities, reflecting the short triplet lifetimes.

5,8-Dimethyltetralone (**3**) was prepared from 4-(2,5-dimethylphenyl)butyric acid by using a procedure similar to that described in the literature for α-tetralone.[25] The crude material was then purified by column chromatography (silica gel using as eluent a 4:1 mixture of petroleum ether and ether) and then recrystallized from petroleum ether; its physical and spectroscopic properties agreed well with those in the literature.[26]

Sample Preparation. The samples (1 mL) were contained in tubes ($3 \times 7 \times 40$ mm) made of Suprasil quartz and were deaerated by bubbling oxygen-free argon. Typical substrate concentrations were in the 0.01-0.04 M range.

Laser Photolysis. The samples were excited by using the pulses from a Molectron UV-400 nitrogen laser. Transient absorptions were detected by using an RCA-4840 photomultiplier tube; the signal was then terminated into 93 ohm and into a Tektronix R7912 transient digitizer which, in turn, has been interphased to a PDP 11/55 computer; further details have been given elsewhere.[18,27]

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Enthalpies of Acetolysis of Tricyclo[3.2.1.0^{1,5}]octane ([3.2.1]Propellane) and 1,3-Dehydroadamantane

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Abstract: The enthalpies of the addition of acetic acid to the [3.2.1]propellane (**1**) and to 1,3-dehydroadamantane (**3**) to give the corresponding bridgehead acetates have been determined. For liquid **1** reacting with liquid acetic acid to give the liquid acetate, $\Delta H_r = -41.18 \pm 0.24$ kcal/mol, and for solid **3** reacting with liquid acetic acid to give the solid acetate, $\Delta H_r = -43.49 \pm 0.08$ kcal/mol. These data have been combined with the enthalpy of the hypothetical addition of acetic acid across an unstrained carbon-carbon single bond to give the strain-energy release on reaction. The values were 55 kcal/mol for **1** and 57 kcal/mol for **3**. The strain energies of **1** and **3** were obtained by adding the strain energies of the products giving for **1** $E_s = 67$ kcal/mol and for **3** $E_s = 64$ kcal/mol.

The small-ring tricyclic compounds commonly known as "propellanes" are of special interest because of their "inverted" tetrahedral geometry in which all four bonds to a bridgehead carbon lie on one side of a plane through the carbon.[2] The hybridization at the bridgehead carbon is close to sp^2 and the central propellane bond is formed by σ overlap of p orbitals.[3] Some of the small-ring propellanes, such as tricyclo[3.2.1.0^{1,5}]octane (**1**), are remarkably reactive toward electrophiles and free radicals,[4] whereas others such as tricyclo[2.2.2.0^{1,4}]octane ([2.2.2]propellane) have remarkable thermal lability.[5]

The heats of formation or the strain energies of these compounds would be useful quantities in interpreting the reactivity data. There are difficulties with carrying out oxygen bomb calorimetry with the propellanes because of their reactivity and/or difficulty of preparation.

Since the small-ring propellanes possessing cyclopropane rings are reactive toward electrophiles, the enthalpy change associated with these reactions provides a means for studying their strain energies. Acetolysis is a convenient reaction, and we have found that tricyclo[3.2.1.0^{1,5}]octane (**1**)[4] and 1,3-dehydroadamantane (**3**)[6] react almost instantaneously at room temperature. The reactions proceed quantitatively to give a single product.

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Table I. Reaction of Tricyclo[3.2.1.0^{1,5}]octane with Acetic Acid

Run no.	E_{calib}	ΔR_{cor}, Ω	R_m, Ω	cal	wt, mg	mol $\times 10^3$	ΔH_{obsd}, kcal/mol	ΔH_{cor},[a] kcal/mol
1	1402.4	5.974	2023.28	4.141	11.70	0.1081	−38.29	−40.62
2	1405.6	8.784	2020.93	6.109	17.30	0.1599	−38.21	−40.54
3	1395.3	22.720	2009.22	15.778	44.38	0.4102	−38.46	−40.81
4	1400.7	13.826	2016.25	9.605	26.94	0.2490	38.57	−40.92
						mean value: −40.72 ± 0.24[b]		

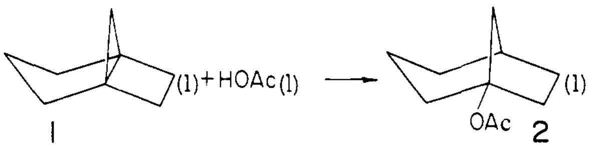
[a] Corrected for 5.75 ± 0.15 mol % nonreacting impurity in 1. [b] Uncertainty is given as $2\bar{s}$ ($\bar{s}$ is the standard deviation from the mean).

Table II. Reaction of 1,3-Dehydroadamantane with Acetic Acid

Run no.	E_{calib}	ΔR_{cor}, Ω	R_m, Ω	cal	wt, mg	mol $\times 10^4$	ΔH, kcal/mol
1	1410.0	8.013	2021.58	5.596	19.35	1.442	−38.81
2	1402.8	8.820	2020.40	6.131	21.14	1.575	−38.92
3	1395.5	8.751	2020.43	6.051	20.87	1.555	−38.92
4	1399.3	7.174	2021.88	4.972	17.11	1.275	−39.00
						mean value: −38.91 ± 0.08[a]	

[a] Uncertainty is given as $2\bar{s}$.

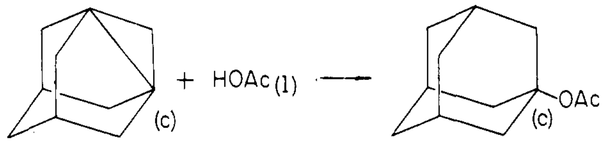
The enthalpies of reaction were determined using an LKB precision calorimetry system. The reaction of **1** in the liquid phase with acetic acid gave $\Delta H_r = -40.72 \pm 0.24$ kcal/mol (Table I). The enthalpy of solution of liquid 1-acetoxybicyclo[3.2.1]octane in acetic acid was found to be +0.46 ± 0.02 kcal/mol. The enthalpy of reaction with all reagents in the liquid phase is then −41.18 ± 0.24 kcal/mol.[7]



1 2

ΔH_r = - 41.18 ± 0.24 kcal/mole

The reaction of 1,3-dehydroadamantane in the solid phase with acetic acid gave $\Delta H_r = -38.91 \pm 0.08$ kcal/mol (Table II). The enthalpy of solution of solid 1-acetoxyadamantane (**4**) in acetic acid was found to be 4.58 ± 0.02 kcal/mol. The enthalpy of reaction of solid **3** with liquid acetic acid to give solid **4** is then −43.49 ± 0.08 kcal/mol. Most of the heat of solution of **4** results from the heat of fusion. Adamantane should be a reasonable model for **3**, and its enthalpy of solution was 4.38 ± 0.03 kcal/mol. The similarity of the two enthalpies of solution indicates that enthalpy of reaction with all species in the liquid phase should not differ significantly from the value given above.



3 4

ΔH_r = - 43.49 ± 0.08 kcal/mole

In order to derive strain energies from the enthalpies of reactions, it is necessary to have data for the corresponding reaction of a strain-free model system. The hypothetical reactions shown in Table III represent relatively strain-free cases, and the enthalpies may be obtained from the known heats of formation. The average value is 13.6 kcal/mol.

When the enthalpy of reaction of **1** is corrected for the enthalpy of the model reaction, the strain relief accompanying acetolysis is found to be 55 kcal/mol. The strain energy of bicyclo[3.2.1]octane has been estimated to be 12 kcal/mol,[9] giving a total strain energy of 67 kcal/mol for **1**. This is in good agreement with the estimate of 60–66 kcal/mol for the strain energy of 8-oxatricyclo[3.2.1.0^{1,5}]octane derived from its enthalpy of combustion.[10]

Table III.[8] Enthalpies of C–C Bond Cleavage by Acetic Acid

reaction	ΔH_r(l), kcal/mol
$C_2H_5C_2H_5 + HOAc \rightarrow C_2H_6 + C_2H_5OAc$	14.3
$(CH_3)_2CHCH(CH_3)_2 + HOAc \rightarrow (CH_3)_2CH_2 + (CH_3)_2CHOAc$	12.9
	av 13.6

The strain relief accompanying the acetolysis of **3** may be obtained in the same fashion, giving a value of 57 kcal/mol. The strain energy of adamantane has been estimated as 6.5 kcal/mol,[11] giving the total strain in **3** as 64 kcal/mol. The close similarity in the strain relief accompanying the cleavage of the central bonds in **1** and **3** corresponds well with the close similarity in the reactions of the two hydrocarbons.[4,6]

Reactions of this type which lead to the cleavage of carbon-carbon bonds should prove of general utility in determining the strain relief accompanying a reaction. Unfortunately, most cyclopropanes will not react with acetic acid at a rate compatible with our reaction calorimeter. Preliminary studies suggest that trifluoroacetic acid may be of more general utility for this process.

Experimental Section

Tricyclo[3.2.1.0^{1,5}]octane (1). The compound was prepared as described previously[4] and was purified by gas chromatography. Analysis by GC using a ⅛ in. × 21 ft 3% OV-17 column at 80°C indicated the presence of 2% of an impurity with a slightly shorter retention time (22.5 min) than that of **1** (25 min). When **1** was treated with acetic acid, the impurity was found to be unchanged. However, a second impurity (4%) was now found with a retention time equal to that of **1**. Quantitative analysis of the reaction solutions using octane as an internal standard indicated 1.93 ± 0.14% of the first impurity and 3.82 ± 0.06% of the second giving 5.75 ± 0.15% as the total unreactive impurity. This assumes that the second impurity was initially present and not a reaction product. Since the acetate derived from **1** has a considerably longer GC retention time than the reactant, it is unlikely that the second impurity is another acetate. It could be an alkene formed by acid-catalyzed rearrangement of **1**, but, in view of previous work on the reaction of **1**,[4] this appears unlikely. The intervention of such a reaction, with a somewhat smaller ΔH_r than the addition of acetic acid, would lead to an observed ΔH_r which is somewhat smaller than the true value.

Since **1** reacts with oxygen in air, it was transferred under nitrogen from the GC collection vessel to the calorimeter ampule which was quickly sealed. The sample weights ranged from 12 to 44 mg.

1-Acetoxybicyclo[3.2.1]octane (2). The addition of 1.0 g of **1** to 7 mL of dry acetic acid was followed by the addition of 20 mL of ether and neutralization with saturated sodium carbonate solution. After drying over magnesium sulfate, the ether was carefully removed through a 24-cm column packed with glass beads. Analysis of the ether distillate indicated that the two impurities had not distilled. The reaction product was analyzed for the amounts of the impurities. In order to obtain a pure sample of **2**, the product was warmed under reduced pressure for 2 h. The material thus obtained was indicated to be pure by GC and was used for the enthalpy of solution measurements.

1,3-Dehydroadamantane (3). The hydrocarbon was prepared as described previously[6] and was stored as an ether solution under oxygen-free nitrogen. It was separated from the solvent using a 3/8 in. × 15 ft 18% Carbowax column at 90 °C, and the hydrocarbon was collected directly into a calorimeter ampule, which was then sealed. The samples were on the order of 20 mg. One ampule was broken in a vial containing dry acetic acid. Analysis of the product indicated only one compound, 1-acetoxyadamantane.

1-Acetoxyadamantane (4). The acetate was prepared by the reaction of 1-hydroxyadamantane with acetic anhydride.[12] After distillation (bp 118 °C at 16-17 mm) it crystallized to give **4**, mp 31-31.5 °C (lit.[11] 33-34 °C). Analysis by GC showed a single product, identical with that obtained from the reaction of **3** with acetic acid.

Calorimetric Studies. The enthalpies of reaction and solution were determined using an LKB 8700 calorimetric system.[13] The calorimeter was checked using the enthalpy of solution of Tris (tris(hydroxymethyl)aminomethane) in 0.100 N hydrochloric acid. The average of seven runs was −7113 ± 5 cal/mol, in good agreement with the accepted value,[14] −7115 ± 8 cal/mol.

In a typical calorimetric run, resistance data were collected during a 5-min foreperiod, a 5-min main period following ampule breaking, and a 5-min afterperiod. The reaction half-lives were less than 30 s. The foreperiod and afterperiod data were separately fitted to the equation

$$R = at^3 + bt^2 + ct + d$$

where t is time using the method of least squares. The root mean square error was on the order of $1\text{-}5 \times 10^{-3}\ \Omega$, which corresponds to about $1\text{-}5 \times 10^{-5}$ deg. The resistance change during the main period was obtained from the least-squares solutions. The resistance correction due to stirring and thermal leakage was calculated by numerical integration of Newton's equation

$$dT/dt = a_1 + a_2T + a_3T^2$$

where the last term was added to correct for any nonlinear effects. In terms of resistance this becomes

$$dR/dt = R[c_1(\ln R)^2 + c_2 \ln R + c_3]$$

The constants c_1, c_2, and c_3 were determined by fitting the data for both the fore- and afterperiods to the equation. Integration over the main period using these constants gave the temperature correction.

An electrical calibration was carried out for each calorimetric run.

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Hydrolysis of Strained Bridgehead Bicyclic Vinyl Ethers and Sulfides

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Abstract: Rates of hydrolysis of the bridgehead bicyclic vinyl ether 9-oxabicyclo[3.3.1]non-1-ene (**6**) and its vinyl sulfide counterpart 9-thiabicyclo[3.3.1]non-1-ene (**7**), catalyzed by the hydronium ion, were measured in H_2O and in D_2O solution. These data give isotope effects, $k_H/k_D = 2.4$ and 1.9 respectively, which show that these reactions occur by the normal, rate-determining carbon protonation, mechanism. The vinyl ether **6** is less reactive than its olefin analogue, bicyclo[3.3.1]non-1-ene (relative rates $1{:}{}^1/_{1400}$), as may have been expected for a constrained bicyclic system such as this, where stabilization of the bridgehead carbocation intermediate by conjugation with oxygen is severely impaired. The vinyl sulfide **7**, however, is even less reactive than the vinyl ether (relative rates $1{:}{}^1/_{140}$); this is a remarkable result in view of the fact that conjugation between the sulfur atom and the cationic center is presumably also strongly inhibited.

The reactivity of vinyl ethers to electrophilic addition is generally very much greater than that of the corresponding olefins. For example, protonation of methyl cyclohexenyl ether (**1**), as determined by its rate of hydrolysis,[3] occurs 1.4×10^5 times faster than protonation of 1-methylcyclohexene (**2**), as measured by its rate of hydration;[4] for the methyl vinyl

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