

Electrophilic Cleavage of Cyclopropanes. Acetolysis of Bicyclic and Tricyclic Cyclopropanes

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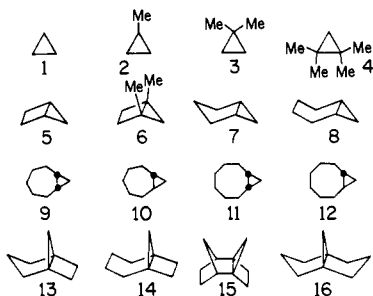
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Abstract: The acetolysis of a series of bicyclo[*n*.1.0]alkanes and [*n*.*m*.1]propellanes has been studied. The effect of ring strain, caused by changing ring size or introducing a trans-ring fusion, on the rate and products of the reaction has been examined. No correlation was found between rates of acetolysis and strain energy relief, but with the exception of [3.2.1]propellane, there is a rough correlation with ionization potentials. The degree of polarization of the C-C bonds in the presence of a proton correlates very well with reactivity and is a controlling factor for the acetolysis rates. The importance of the energies of unoccupied orbitals with the appropriate symmetry in controlling electron polarization is shown by the large difference in rate of reaction between [3.2.1]- and [4.2.1]propellanes.

The two preceding papers in this issue have been concerned with the effects of alkyl substitution on the rates, regiochemistry, and stereochemistry of the acetolysis of cyclopropanes¹ and with the nature of the process involved in the acetolysis of bicyclo-[2.1.0]pentane.² The results indicated that the reaction proceeds toward the formation of the most stable carbocation via rate-determining protonation, that the protonated cyclopropane reacts with the solvent, acting as a nucleophile before it is cleaved to form an open carbocation, and that both strain energy relief and the stability of the incipient carbocation have only a small effect on the rate of reaction. We have continued this study by examining the rates of acetolysis of a series of bicyclo[*n*.1.0]alkanes³ as well as [3.2.1]propellane.⁴ We also have made use of data in the literature on the rates of cleavage of related compounds such as [4.2.1]propellanes.⁵

The compounds of interest are 1-16. Rate constants for 1-6 have been given,^{1,2} data for 14 and 16 were given by Warner⁵ et al., and data for 13 and 15 were reported by Reynolds.⁶ The rate constants for 7-12 are given in Table I, and the products are shown in Scheme I.

The internal bond is preferentially cleaved in only two of the bicyclic cases, 5 (6) and 10. Here, the large strain energy relief on going toward a stretched carbocation is sufficient to divert the reaction from its normal course. In all other cases, protonation



occurs preferentially at the cyclopropyl methylene group, leading to a methyl-substituted cycloalkyl cation. Bicyclo[3.1.0]hexane

Table I. Rates of Acid-Catalyzed Acetolysis, 0.005 M TsOH

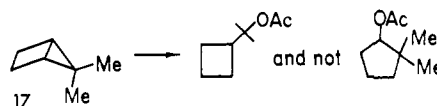
compound	temp, °C	$k \times 10^5$, s ⁻¹	ΔH^\ddagger , kcal/mol	ΔS^\ddagger , eu
bicyclo[3.1.0]hexane (7)	60.00	0.98	16.2	-33
	45.00	0.285		
bicyclo[4.1.0]heptane (8)	80.12	11.9	15.9	-32
	60.00	2.85		
<i>cis</i> -bicyclo[5.1.0]octane (9)	100.40	24.9	17.1	-30
	80.00	6.20		
<i>trans</i> -bicyclo[5.1.0]octane (10) ^a	60.00	23.8	18.8	-19
	45.00	5.98		
<i>cis</i> -bicyclo[6.1.0]nonane (11)	99.95	25.9	16.9	-30
	80.05	6.78		
<i>trans</i> -bicyclo[6.1.0]nonane (12)	99.98	22.9	17.5	-29
	80.05	5.71		

^aIn this case it is possible that some internal return to a tosylate occurred which would not undergo solvolyses rapidly enough to ensure a constant concentration of acid catalyst. Thus, the observed rate constants should be considered to be minimum values.

is an intermediate case which gives 30% internal cleavage and 70% external cleavage.

With the polycyclic cyclopropanes, central bond cleavage occurs in the cases having a bicyclo[2.1.0]pentane nucleus.⁴⁻⁶ Again, this is probably due to the large degree of strain energy relief which is found with these compounds. [3.3.1]Propellane (16) undergoes both internal and external cleavage,⁵ similar to that found with the related bicyclo[3.1.0]hexane (7).

In a number of cases, the products do not represent the thermodynamically expected ratio. With 7, cleavage of the internal bond would relieve all the strain whereas cleavage of the other cyclopropane C-C bonds would lead to a cyclopentane derivative which relieves less of the strain energy. Nevertheless, external cleavage is preferred. In an extreme example, 5,5-dimethylbicyclo[2.1.0]pentane (17) reacts to form a cyclobutane derivative rather than a cyclopentane derivative despite the much larger strain relief in the latter case.² A comparison of the rates of reaction



of 5 and 7 suggested that only ~10% of the potential strain relief was found in the activated complex for the rate-determining step. It is clear that strain energy relief is only one of several factors which control the products of reaction, and it is one of the less important factors. Stabilization of the developing carbocation is probably a more important factor.

The relative rates of reaction of the cyclopropanes are summarized in Table II. We should like to understand the factors which control the rates. Despite the apparently limited role of

(1) Wiberg, K. B.; Kass, S. R. *J. Am. Chem. Soc.*, first of three papers in this issue.

(2) Wiberg, K. B.; Kass, S. R.; Bishop, K. C. *J. Am. Chem. Soc.* preceding paper in this issue.

(3) For preliminary accounts of these studies see: Wiberg, K. B.; de Meijere, A. *Tetrahedron Lett.* 1969, 519. Wiberg, K. B.; Bishop, K. C., III; Davidson, R. B. *Tetrahedron Lett.* 1973, 3169.

(4) Wiberg, K. B.; Connon, H.; Pratt, W. J. *J. Am. Chem. Soc.* 1979, 101, 6970.

(5) Warner, P.; LaRose, R.; Schleis, T. *Tetrahedron Lett.* 1974, 1409. Warner, P.; LaRose, R. *Ibid.* 1972, 2141.

(6) Reynolds, R. N. Ph.D. Thesis, University of California, Santa Barbara, 1977.

Table II. Relative Rates of Acetolysis of Cyclopropanes

compound	k_{rel}	$\log k_{rel}$	IP ^a	ΔSE^b
tetracyclo[4.2.1.1 ^{2,5} .0 ^{1,6}]dodecane (15)	1.9×10^6	6.3		
[3.2.1]propellane (13)	1.2×10^6	6.1	8.41	58
[4.2.1]propellane (14)	93	2.0	8.50	48
5,5-dimethylbicyclopentane (17)	79	1.9		28
1,4-dimethylbicyclopentane (6)	2	0.30	8.8	51
bicyclo[2.1.0]pentane (5)	1.0	0.0	9.55	51
[3.3.1]propellane (16)	0.36	-0.44		29
1,1,2,2-tetramethylcyclopropane (4)	0.29	-0.54	9.18	28
<i>trans</i> -bicyclo[5.1.0]octane (10)	0.27	-0.57		33
1,1-dimethylcyclopropane (3)	0.065	-1.2	9.72	28
bicyclo[4.1.0]heptane (8)	0.032	-1.5	9.46	27
<i>cis</i> -bicyclo[6.1.0]nonane (11)	0.018	-1.7		24
<i>cis</i> -bicyclo[5.1.0]octane (9)	0.017	-1.8		23
<i>trans</i> -bicyclo[6.1.0]nonane (12)	0.015	-1.8		25
bicyclo[3.1.0]hexane (7)	0.011	-2.0	9.65	27
methylcyclopropane (2)	5.6×10^{-3}	-2.3	10.1	28
cyclopropane (1)	4.9×10^{-5}	-4.3	10.9	28

^aReference 10. ^bReference 7. The values do not take into account the difference in energy between secondary and tertiary carbocations.

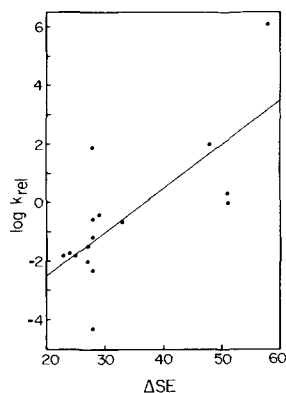


Figure 1. Relationship between the logarithms of the relative rates of acetolysis and the strain energy relief in the reaction. The slope, 0.15, corresponds to about 10% of the strain relief being available to reduce the free energy of activation. The correlation coefficient is only 0.75.

strain energy relief in determining the products of reaction, it appeared prudent to examine the possible effect on the rates of reaction of this larger group of compounds. The strain energies of the reactants are fairly well-known, and the strain energies of the products may be approximated by the strain energies of the corresponding hydrocarbons.⁷ However, the species formed in the rate-determining step might be better approximated by a carbocation rather than the acetate product. The rates of solvolysis of cyclopentyl, cyclohexyl, cycloheptyl, and cyclooctyl tosylates vary considerably.⁸ Thus, cyclopentyl tosylate is more reactive than cyclohexyl tosylate because of the relief of torsional strain on going to the cation. Relative to cyclohexyl, the cyclopentyl cation appears to be stabilized by 2 kcal/mol, cycloheptyl cation by 1 kcal/mol, and cyclooctyl by 2 kcal/mol.⁸ With these corrections, we obtain the strain energy relief shown in Table II.

(7) The strain energies of the reactants were taken as (kcal/mol) 1, 27.5; 2, 27.5; 3, 27.5; 4, 27.5; 5, 54.7; 6, 54.7; 7, 31.1; 8, 27.2; 9, 27.7; 10, 39.8; 11, 31.6; 12, 32.1; 13, 67; 14, 65 (estimated); 16, 35 (estimated); 17, 54.7 (Wiberg, K. B.; Lupton, E. C., Jr.; Wasserman, D. J.; de Meijere, A.; Kass, S. R. *J. Am. Chem. Soc.* **1984**, *106*, 1740. Wiberg, K. B. *Ibid.* **1983**, *105*, 1227). The strain energies of the product acetates were taken to be the same as those of the corresponding hydrocarbons (the numbers correspond to the reactants from which they were obtained): 1, 0.0; 2, 0.0; 3, 0.0; 4, 0.0; 5, 6.1; 7, 6.1; 8, 0.0; 9, 6.1; 10, 9.2; 11, 9.2; 12, 9.2; 13, 9; 14, 17; 16, 6; 17, 26 (Wiberg, K. B. In "Determination of Organic Structures by Physical Methods"; Nachod, F. C., Zuckerman, J. J., Ed.; Academic Press: New York, 1971; Vol. 3, p 238. Engler, E. M.; Andose, J. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1973**, *95*, 8005.

(8) Roberts, J. D.; Chambers, V. C. *J. Am. Chem. Soc.* **1951**, *73*, 5034.

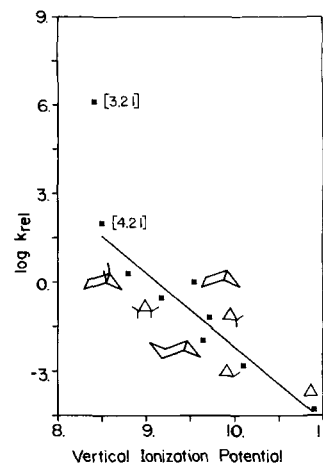


Figure 2. Relationship between the logarithms of the relative rates of acetolysis and the first vertical ionization potentials of the cyclopropanes.

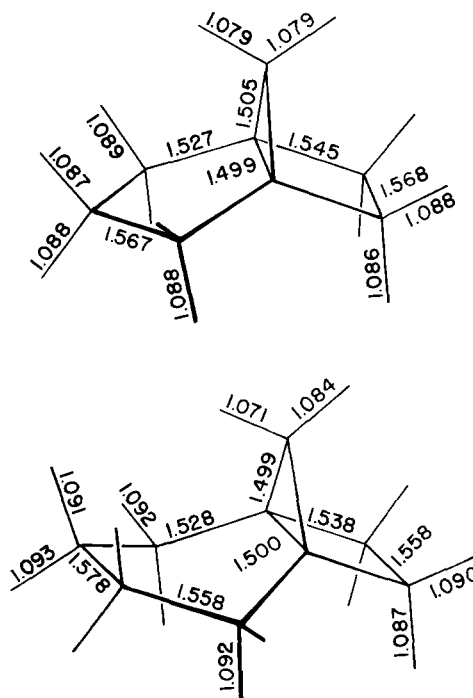


Figure 3. STO-3G optimized geometries for [3.2.1]propellane (upper) and [4.2.1]propellane (lower).

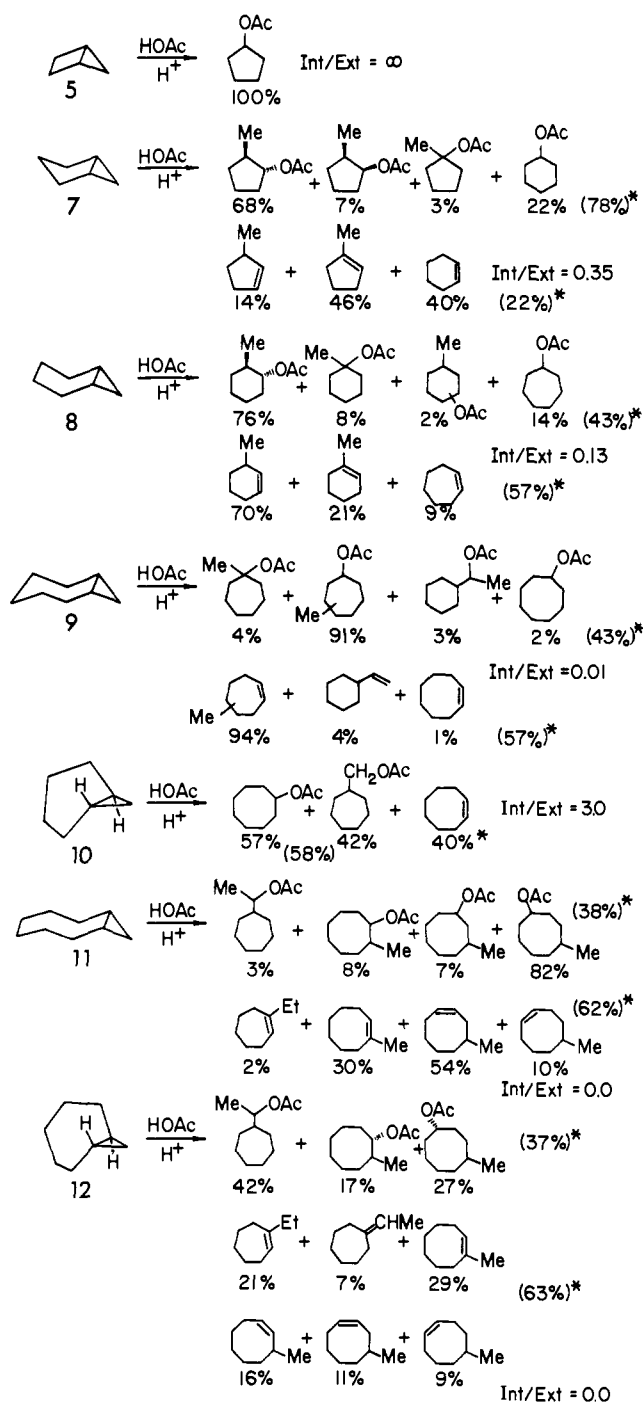
A plot of $\log k_{rel}$ against ΔSE is shown in Figure 1. It can be seen that there is a poor correlation, indicating that strain relief is not an important factor in determining reactivity. The observations that proton transfer occurs in the rate-determining step for these reactions and that strain relief is not important indicate that structural changes are relatively small on going to the activated complex.

The stability of the incipient carbocation is important in determining the acetolysis products, and therefore its influence on the relative rates needs to be considered. However, 5 and 6 have been found to have rates of reaction which differ only by a factor of 2 despite the fact that they form incipient secondary and tertiary carbocations, respectively. In addition, propellanes 13–16 all react to give incipient tertiary carbocations but span a range of approximately 10^7 in reactivity. It is clear that carbocation stability is not the important factor in determining the rates of reaction.

Another possible way in which the changes in rate may be correlated is via a frontier orbital approach.⁹ Here, one would consider the interaction of the empty s orbital at the proton with the highest occupied molecular orbital of the cyclopropane de-

(9) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57.

Scheme I



*percent of total products

rivative. A correlation of $\log k_{\text{rel}}$ with the first vertical ionization potential¹⁰ is shown in Figure 2. A fair correlation is found if one ignores [3.2.1]propellane. The ionization potentials of [3.2.1]- and [4.2.1]propellanes are essentially the same despite the 10^4 difference in reactivity. What is the source of the large difference in reactivity between these two propellanes?

One possible factor is the difference in strain energy relief. However, we have shown that this is not normally an important factor. What other factors may be involved? In order to see if there were any obvious differences in the electronic structures, electron density distributions were calculated by using 3-21G wave functions calculated at the STO-3G optimized geometries (Figure 3),¹¹ and again no significant difference was found either in the

(10) Gleiter, R. *Top. Curr. Chem.* **1979**, *86*, 196. Bischof, P.; Heilbronner, E.; Prinzbach, H.; Martin, H. D. *Helv. Chim. Acta* **1971**, *54*, 1072.

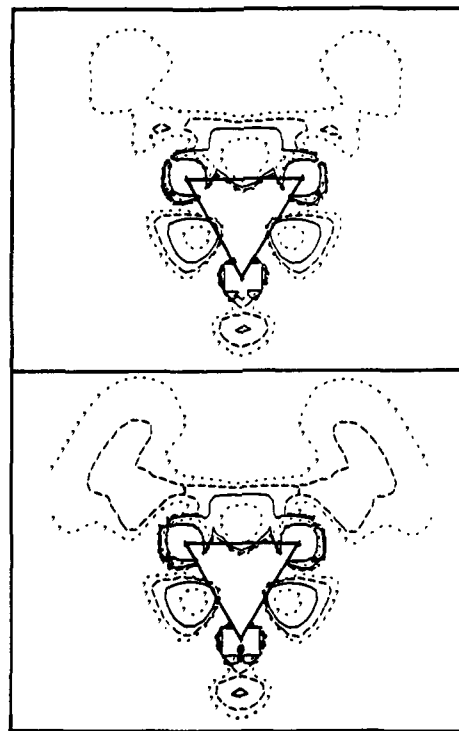


Figure 4. Deformation densities for the cyclopropane rings of [3.2.1]-propellane (upper) and [4.2.1]propellane (lower) calculated by using the 3-21G basis set. The contours are (from outer to inner) 0.0032 (short dash), 0.0063 (long dash), 0.0125 (solid), and 0.025 (short dash) e/bohr^3 .

Table III. Electron Populations at the Attacking Proton

compound	population	$\log k_{\text{rel}}$
cyclopropane (1)	0.377	-4.3
bicyclo[3.1.0]hexane (7)	0.399	-2.0
bicyclo[2.1.0]pentane (5)	0.419	0.0
5,5-dimethylbicyclo[2.1.0]pentane (17)	0.439	1.9
[3.2.1]propellane (13)	0.514	6.1

densities themselves or in the deformation densities (i.e., the difference between the electron densities and those for spherically symmetrical atoms at the corresponding locations) (Figure 4).

It is reasonable to assume that the proton initially attacks one of the bridgehead carbons in these compounds.¹² An important consideration is how well the central C-C bond may become polarized so as to transfer electron density to the incoming proton. This was calculated as follows. A proton was placed 2 Å away from the bridgehead carbon along the extension of the line formed by the bridgehead-bridgehead bond, which should correspond roughly to the direction of attack. The wave functions were calculated by using the STO-3G basis set, which is as large as practical with these large unsymmetrical species. The geometries for the hydrocarbons were the optimized STO-3G structures. The electron population at the incoming hydrogen was calculated by obtaining the partitioning surface for the CH bond as defined by Bader¹³ and then integrating the square of the wave function in

(11) The STO-3G geometry for [3.2.1]propellane is generally in good agreement with the experimental structure of the 7,7-dichloro derivative (Wiberg, K. B.; Burgmeier, G. J.; Shen, K.-W.; La Placa, S. J.; Hamilton, W. C.; Newton, M. D. *J. Am. Chem. Soc.* **1972**, *94*, 7402) except for the central C-C bond and the parallel cyclobutane bond. It is not clear to what extent the chlorines affect the structure (cf. for substituent effects on cyclopropane rings: Dill, J. D.; Greenberg, A.; Liebman, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 6814). The questions of the structures of these propellanes and of the reasons for the differences in energies of the antisymmetric virtual orbitals (Table IV) are receiving continued attention.

(12) Both [3.2.1]- and [4.2.1]propellane react exclusively by cleavage of the central C-C bond.^{4,6} Since the bridgehead carbons are additionally bonded to three other carbons, the only possible direction of attack is roughly along the axis of the central C-C bond. Bicyclo[2.1.0]pentane also reacts by cleavage of the central bond.

Table IV. Orbital Energies for Cyclopropyl Derivatives

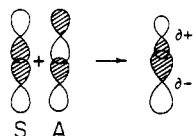
orbital	compound					
	13	14	17	5	7	1
n (HOMO)	-0.3432 (S)	-0.3413 (S)	-0.3653 (S)	-0.3735 (S)	-0.3855 (S)	-0.3846 (S)
$n + 1$ (LUMO)	+0.2496 (S)	+0.2415 (S)	+0.2662 (S)	+0.2696 (S)	+0.2603 (S)	0.4956 (A)
$n + 2$	+0.2682 (S)	+0.2692 (S)	+0.2754 (S)	+0.2914 (A)	+0.2743 (S)	0.5706 (S)
$n + 3$	+0.2768 (A)	+0.2903 (S)	+0.2839 (A)	+0.2970 (S)	+0.3153 (A)	0.6792 (S)
$n + 4$	+0.2953 (S)	+0.2937 (A)	+0.2957 (S)	+0.3123 (S)	+0.3207 (S)	0.7133 (S)
$E_A - E_{\text{HOMO}}$	0.6200	0.6350	0.6492	0.6649	0.7008	0.8802
$\log k$	6.1	2.0	1.9	0.0	-2.0	-4.3

Table V. Electron Populations on a per Molecular Orbital Basis

orbital	compound				
	1	7	5	17	13
n (HOMO)	0.177 (47%)	0.125 (31%)	0.252 (60%)	0.179 (41%)	0.278 (54%)
$n - 1$	0.075 (20%)	0.009	0.003	0.088 (20%)	0.000
$n - 2$	0.000	0.003	0.019 (5%)	0.000	0.001
$n - 3$	0.003	0.003	0.002	0.014 (3%)	0.007
$n - 4$	0.051 (14%)	0.091 (23%)	0.003	0.001	0.005
$n - 5$	0.002	0.009	0.003	0.001	0.045 (9%)
$n - 6$	0.000	0.009	0.003	0.001	0.001
$n - 7$	0.063 (17%)	0.002	0.041 (10%)	0.000	0.001
$n - 8$	0.003	0.005	0.014 (3%)	0.008 (2%)	0.072 (14%)
$n - 9$	0.000	0.036 (9%)	0.036 (9%)	0.004	0.003
$n - 10$	0.000	0.022 (6%)	0.011 (3%)	0.035 (8%)	0.002
$n - 11$	0.000	0.026 (7%)	0.032 (8%)	0.005	0.009 (2%)
$n - 12$		0.012 (3%)	0.000	0.015 (3%)	0.011 (2%)
$n - 13$		0.012 (3%)	0.002	0.000	0.018 (4%)
$n - 14$		0.026 (7%)	0.000	0.050 (11%)	0.007
$n - 15$		0.003	0.000	0.016 (3%)	0.000
$n - 16$		0.004	0.000	0.029 (7%)	0.006
$n - 17$		0.000	0.000	0.002	0.003
$n - 18$		0.000	0.000	0.001	0.010 (2%)
$n - 19$		0.000	0.000	0.002	0.014 (3%)
$n - 20$		0.000	0.000	0.000	0.003
total	0.377	0.399	0.419	0.439	0.514

the region from the surface toward the hydrogen and then on to infinity. The values are given in Table III. It was not possible to include [4.2.1]propellane in this study because a methylene group of the six-membered ring was found to be very close to the incoming proton as defined above. Nevertheless, a plot of $\log k_{\text{rel}}$ against the electron population is linear and reasonably correlates the rate of reaction of [3.2.1]propellane with that of the other compounds (Figure 5). Thus, polarization appears to be one of the more important factors controlling the rate of reaction.

Why should polarization of the central bond of [3.2.1]propellane be more facile than that of the other compounds? The highest occupied MO is symmetric with respect to the plane of symmetry and has a large coefficient for the orbitals forming the central bond. Polarization of this bond requires mixing with an empty orbital which is antisymmetric; Thus, polarization depends in



considerable measure on the difference in energy between the two orbitals. The calculated energies of the highest occupied molecular orbitals along with the energies of some of the lower energy unoccupied orbitals are given in Table IV. The LUMO is symmetric in all cases and is not involved. The first antisymmetric orbital varies considerably in its order, and it can be seen that there is a general agreement between $E_{\text{HOMO}} - E_{\text{A}}$ and the relative reactivity. One would not expect a simple linear relationship because the energy gap is related only to the initial polarization

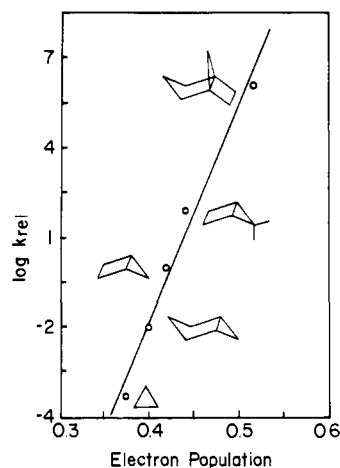


Figure 5. Relationship between the logarithms of the relative rates of acetolysis and the calculated electron populations at the attacking proton 2 Å from a ring carbon.

and not to the large perturbation produced by a proton 2 Å from the bridgehead carbon. Nevertheless, this points out the importance of polarization in considering reactions in which charged species interact with neutral molecules.

The integration of the electron density transferred to the proton can be done on an orbital-by-orbital basis and allows one to see to what extent the highest occupied MO is involved in the transfer (Table V). It can be seen that only ~50% of the density comes from the HOMO and that much of it comes from relatively low-lying orbitals. Thus, although frontier orbital theory gives a rough correlation with the rates of acetolysis for most cyclopropanes, it does not give a very accurate representation of the reaction.

(13) Srebrenik, S.; Bader, R. F. W.; Nguyen-Dang, T. T. *J. Chem. Phys.* **1978**, *68*, 3667. Bader, R. F. W.; Anderson, S. G.; Duke, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 1389.

In all cases except 5,5-dimethylbicyclo[2.1.0]pentane, the direction of charge transfer was essentially along the line connecting the bridgehead carbons with the attacking proton. In this case, however, a large component was found to lie along the bond from the bridgehead carbon to the CMe₂ carbon, and this probably accounts for the change in which bond is broken.

The nature of these reactions may then be summarized as follows. Proton transfer is rate determining, and the rate of proton transfer depends on the ease of polarization of one (or more) of the carbon-carbon bonds. The reaction proceeds toward the more stable carbocation, but at the product forming activated complex, the structure has not relaxed to a large degree as indicated by the small role of strain relief. The products are formed in major extent by capture of the protonated species before it becomes an open carbocation, leading to stereoselective capture by the nucleophile, and stereoselective hydrogen migration or loss.

Experimental Section

Materials. The *cis*-bicyclo[*n*.1.0]alkanes were prepared by the addition of methylene to the corresponding cycloalkene.¹⁴ *trans*-Bicyclo[5.1.0]octane and *trans*-bicyclo[6.1.0]nonane¹⁵ were prepared by using published procedures. In each case, the compound was purified by preparative scale gas chromatography. Acetic acid was dried as described previously.¹

Kinetics. A solution of 0.4740 g of *p*-toluenesulfonic acid monohydrate and 5.623 g of chlorobenzene (internal standard) in acetic acid containing

1% acetic anhydride was prepared. Solutions of the cyclopropanes in this solvent were prepared and small aliquots were sealed into ampules. The ampules were placed in a thermostat and were allowed to equilibrate for 5-10 min. The timer was started, and ampules were removed at appropriate intervals and cooled in ice. They were opened and quenched with sodium acetate in acetic acid. Analysis was performed by GC using either a 50-ft Carbowax 20M or a 30-ft Squalene column and a flame ionization detector. The ratio of unchanged hydrocarbon to internal standard was determined by using a H-P digital integrator.

Isotope Effect. [3.2.1]Propellane reacts with acetic acid at 25 °C with a half-life of about 5 s.⁴ Therefore, it was not practical to determine the solvent isotope effect by separate rate measurements. A small sample of **13** was added to a mixture of 48% HOAc and 52% DOAc. The product, 1-bicyclo[3.2.1]octyl acetate was examined by ¹H and ²H NMR spectroscopy which indicated 79% *d*₀ and 21% *d*₁. The mass spectrum, using chemical ionization, was consistent with this analysis.

Calculations. The ab initio calculations were carried out by using the program GAMESS¹⁶ and standard basis sets.¹⁷ The integration of the wave functions to give electron populations was carried out as previously described.¹⁸

Registry No. **1**, 75-19-4; **2**, 594-11-6; **3**, 1630-94-0; **4**, 4127-47-3; **5**, 185-94-4; **6**, 17065-18-8; **7**, 285-58-5; **8**, 286-08-8; **9**, 16526-90-2; **10**, 21370-66-1; **11**, 13757-43-2; **12**, 39124-79-3; **13**, 19074-25-0; **14**, 38325-64-3; **15**, 53797-19-6; **16**, 27621-61-0.

(14) Dupuis, M.; Spangler, D.; Wendoloski, J. J. National Resource for Computation in Chemistry Program QG01, 1980.

(17) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657. Ditchfield, R.; Hehre, W. J.; Pople, J. A. *Ibid.* **1971**, *54*, 724.

(18) Wiberg, K. B.; Wendoloski, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 6561.

(14) Rawson, R. J.; Harrison, I. T. *J. Org. Chem.* **1970**, *35*, 2057.

(15) Wiberg, K. B.; de Meijere, A. *Tetrahedron Lett.* **1969**, 519. Wiberg, K. B.; Lupton, E. C., Jr.; Wasserman, D. J.; de Meijere, A.; Kass, S. R. *J. Am. Chem. Soc.* **1984**, *106*, 1740.

Stable Simple Enols. 8.¹ Synthesis and Keto \rightleftharpoons Enol Equilibria of the Elusive 2,2-Dimesitylethanal and 1,2,2-Trimesitylethanone. Conformations of 1,2,2-Trimesitylethanone and 1,2,2-Trimesitylethanol

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Abstract: 2,2-Dimesitylethanal (**2**) and 1,2,2-trimesitylethanone (**4**) were prepared by pyridinium dichromate oxidation of 2,2-dimesitylethanol (**5**) and 1,2,2-trimesitylethanol (**7**), respectively. For **4**, $\epsilon = 11\,000$ in hexane at 250 nm, $\delta(^{13}\text{C}=\text{O}) = 204.65$ ppm, and $\nu_{\text{CO}} = 1688, 1695$ cm⁻¹, indicating a substantial conjugation between the α -mesityl and the C=O moieties. The calculated dihedral angle Mes-CO θ is 39° and the observed value in the solid is 48°. Other triarylethanones show similar effects. Consequently, bulky β substituents on crowded α -aryl ketones can reduce, rather than increase, the Mes-CO angle. The conformation of **4** is "bisected" with a H-C-C-O angle of ca. 180°, and the three rings adopt a propeller conformation. At 210 K the two β -mesityl groups of **4** are magnetically equivalent, but the α ring *o*-Me and *m*-H protons and the corresponding carbons are anisochronous. A DNMR study suggests that the rapid rotational process which equalizes the β -mesityl groups is a two-ring flip with $\Delta G_c^\ddagger < 9.5$ kcal mol⁻¹. The coalescence of diastereotopic groups on the α -ring gives $\Delta G_c^\ddagger = 13.8$ kcal mol⁻¹ for rotation around the Mes-CO bond. Equilibration of **2** and **4** with their enol isomers was followed from both sides in hexane at 353.6 K. The enols consist of >95% in the mixtures and $K_{\text{enol}} = [\text{enol}]/[\text{carbonyl compound}]$ values are 20 ± 1 for **2** and 79 ± 7 for **4**, which are the highest values known for simple enols. They are 9 and 11 orders of magnitude higher than the values for acetaldehyde and acetone. Conformational studies showed that **7** exists in CDCl₃ at 223 K as a 1:1.4 mixture of the *ap* and the *sc* conformers, whereas X-ray diffraction shows that the solid has the *ap* conformation. **7** undergoes a dynamic process at room temperature which was briefly studied.

In a keto \rightleftharpoons enol equilibria of simple carbonyl compounds (i.e., those substituted only by aryl and/or alkyl groups or hydrogen), the keto compounds are usually much more stable. The con-

centrations of the enols are usually so low that they have to be determined indirectly.² Several of the simpler enols, including vinyl alcohol, were recently prepared under kinetic control,³ but

(1) Part 7: Biali, S. E.; Rappoport, Z.; Depke, G.; Eckart, K.; Schwarz, H. *Int. J. Mass Spectrom. Ion Proc.* **1985**, *63*, 289.

(2) (a) For a recent review, see: Toullec, J. *Adv. Phys. Org. Chem.* **1982**, *18*, 1. (b) For a review on stable enols, see: Hart, H. *Chem. Rev.* **1979**, *79*, 515.