

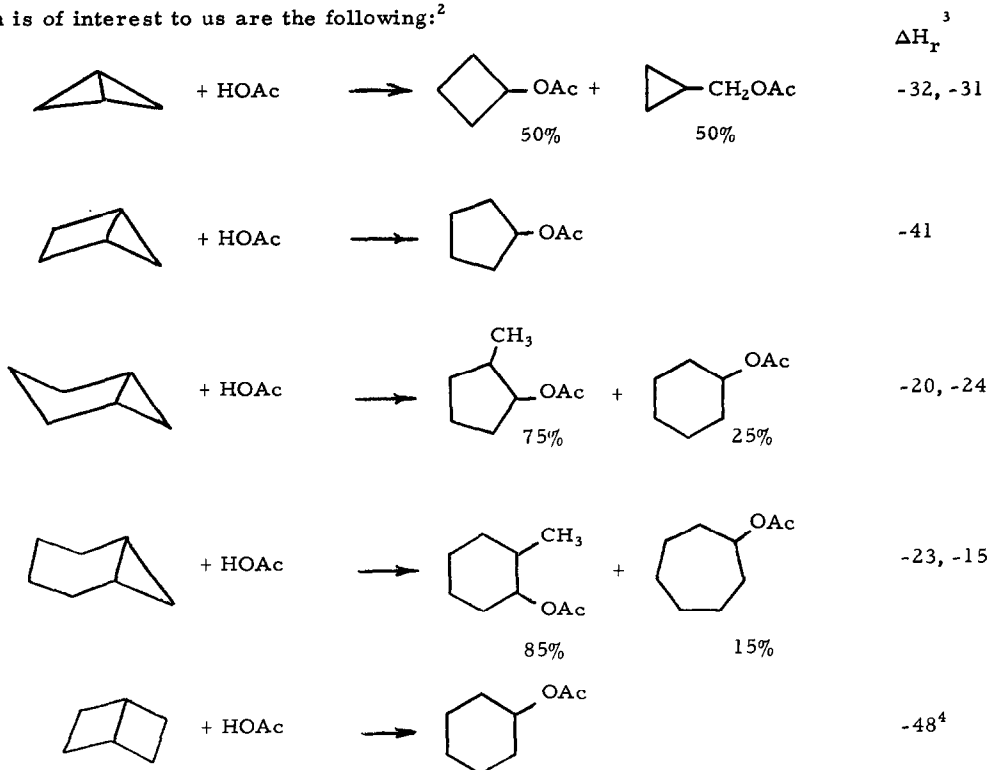
RATE OF ACETOLYSIS OF BICYCLO[2.1.0]PENTANE¹

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(Received in USA 5 June 1973; received in UK for publication 9 July 1973)

It is usually found that with a series of related compounds there is a linear free energy relationship between reactivity and overall energy change. A series of such reactions which is of interest to us are the following:²



Although bicyclo[2.2.0]hexane has led to the most exothermic reaction of this group, it has essentially no reactivity in acid catalyzed acetolysis. This is probably a reflection of the low reactivity of cyclobutanes toward electrophiles.

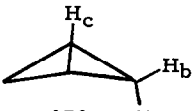
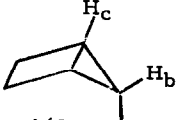
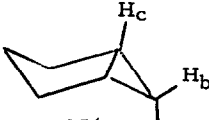
The rates of the acid catalyzed (0.005 M TsOH) acetolyses of the four cyclopropane

derivatives have been determined giving the data in Table 1. Bicyclobutane has such a high reactivity, even without the acid catalyst, that a rate constant could not be determined. With the remaining compounds, bicyclo[2.1.0]pentane is less reactive than bicyclo[4.1.0]heptane rather than more reactive as might be expected from the overall energy change.

Table 1
Rates of Acid Catalyzed Acetolysis

Compound	$k \times 10^5$ (60°)	ΔH^\ddagger	ΔS^\ddagger
Bicyclo[1.1.0]butane	too large to measure		
Bicyclo[2.1.0]pentane	2.13	23.9	-9
Bicyclo[3.1.0]hexane	0.96	16.7	-32
Bicyclo[4.1.0]heptane	2.85	15.9	-32

Two possible explanations of the low reactivity of bicyclo[2.1.0]pentane, despite its favorable heat of reaction, might be: 1, an unusual hybridization or 2, the nature of the higher energy occupied molecular orbitals. The changes in hybridization may be estimated from the C^{13} -H nmr coupling constants:⁵

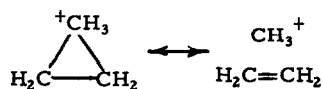
			
$J_{C^{13}-H_a}$	170	162	156
$J_{C^{13}-H_b}$	152	154	156
$J_{C^{13}-H_c}$	203	174	165

It can be seen that for bicyclo[2.1.0]pentane the C-H coupling constants, and hence hybridization is between that found for bicyclobutane and bicyclo[3.1.0]hexane. Thus, the low reactivity does not appear to arise from changes in hybridization.

The low reactivity of bicyclo[2.1.0]pentane may be related to the generally low reactivity of cyclobutanes as compared to cyclopropanes. Thus, with the tricyclic compounds A and B, A reacts rapidly with electrophiles whereas B is relatively unreactive.⁶ It is generally found that the replacement of a cyclopropane ring by a cyclobutane ring results in a decrease in reactivity of 10^6 or larger.



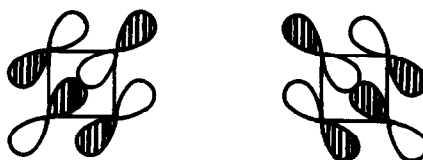
Cyclopropanes react with protons via equilibrium protonation to an edge or corner protonated cyclopropane, followed by nucleophilic attack giving the product. The energies of the two protonated species are similar as indicated by nmr studies.⁷ Whereas a corner protonated cyclopropane has an important contributing structure a methylation-ethylene complex no similar stabilization is found with cyclobutane. CNDO calculations for corner protonated cyclopropane and cyclobutane support this idea.



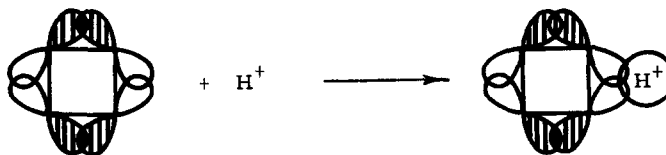
An edge protonated cyclopropane also is a reasonable structure since one member of the degenerate pair of highest bonding MO's is of a suitable form:



However, the highest bonding MO's of cyclobutane are not as hospitable to protonation as they are concentrated along and within the bond axes:^{8,9}



There is, however, another lower energy bonding MO which is of the proper form to participate in a three-center 2-electron bond with a proton:



The energy of an edged protonated cyclobutane is critically dependent on the energy of this orbital and to the extent by which it is involved with binding to the proton. Unfortunately, CNDO calculations on the various protonated species do not appear to be adequate to determine the relative energies of edge protonated cyclopropanes and cyclobutanes.

Regardless of the ultimate explanation, the low reactivity of bicyclo[2.1.0]pentane

toward acid catalyzed acetolysis is in striking contrast to other reactions of this compound. Thus, for example, whereas the rhodium (I) catalyzed isomerization of bicyclo[2.1.0]pentane to cyclopentene proceeds at 60°, no significant isomerization of bicyclo[4.1.0]heptane occurred at 150°. Thus, bicyclo[2.1.0]pentane and bicyclo[4.1.0]heptane appear to be a useful pair of compounds with which to study the difference between reagents which open cyclopropane rings.

References

1. This investigation was supported by a grant from the National Science Foundation.
2. The entropy changes would be expected to be roughly constant, and the free energies of reaction should differ from the heats of reaction by a constant value.
3. The heats of reaction were calculated from available thermochemical data (J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, London (1970). The strain energy of bicyclo[2.2.0]hexane was assumed to be the same as that of bicyclo[2.1.0]pentane, and the group replacement equivalent (cf. K. B. Wiberg in "Determination of Organic Structure by Physical Methods," Vol. III, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, 1971) for acetoxy replacing hydrogen was taken as -89.5 kcal/mole on a cyclic ring.
4. Unlike the previous cases, this reaction has not as yet been effected as a result of its low reactivity.
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