ucts corresponded to unrearranged alcohols and ethers to an extent greater than 90% (by nmr).

The results with V are startling! Instead of the many powers of ten rate enhancement usually associated with cyclopropylcarbinyl systems,[1-3] V reacts almost 10^3 *more slowly* than the model compounds. V is held rigidly in conformation IV. During solvolysis, the developing orbital is constrained to be perpendicular to the cyclopropane ring, *i.e.*, as in II, except for the necessary bending down of the bonds in the adamantane ring. The geometry in V is also not favorable for cyclopropylcarbinyl–cyclobutyl ring expansion nor for ring opening to an allylcarbinyl system. These reactions do not take place either. Thus, there should be no assistance to ionization in V at all, and the solvolysis rate of this compound provides a good indication of what is to be expected in "nonconjugated" II. The observed destabilization and rate depression can be attributed to the electron-withdrawing sp^2 character of the external cyclopropane bonds.[1]

The difference in solvolysis rates between IX (fast) and X (slow) is about $10^{4.3}$ ($n = 5$ and 6).[2] In V, the deceleration is about 10^3. Thus a rough estimate of the energy difference between I and II (in tertiary systems as solvolysis transition states) is 10 kcal/mol, corresponding to a 10^7 rate ratio. In the free ions themselves, this difference might be much larger.[6]

Thus, the stabilization of even a tertiary ion by an adjacent cyclopropane ring is very large, a stabilization which can best be understood in terms of a resonance-type or C–C hyperconjugative interaction,[1,3,4,11] which, of course, is highly geometry dependent.

Acknowledgments. This work was supported by grants from the National Science Foundation, the National Institutes of Health (AI-07766), and the Petroleum Research Fund, administered by the American Chemical Society.

(11) The apparently low methyl:hydrogen ratios, used by Japanese authors as evidence against this interpretation,[2] can be explained in an alternative manner.[12]
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(13) Princeton University Fellow, 1968–1969.

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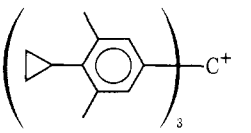
Destabilization of a *t*-Alkyl Cation by an α-Cyclopropyl Substituent. Perpendicularly Twisted Cyclopropylcarbinyl and Allylic Tosylates

Sir:

There is mounting evidence[1-6] that the maximum interaction between a cyclopropyl ring and an adjacent electron-deficient carbon, as in the cations derived from cyclopropyl carbinols, occurs when the plane of the three-membered ring is parallel to the adjacent p orbital, *i.e.*, the "bisected"[1,6] conformation or its equivalent.[5]

This has been shown in equilibrium studies[2] (pK_{R^+} of triarylcarbinols) and rate studies[3] (cumyl chloride solvolyses) in systems such as **1** in which the flanking *o*-methyls prevent the attainment of the bisected geometry by the cyclopropyl ring, making it even less electron releasing than the isopropyl group. The nmr chemical shift evidence[2] for a substantial residue of charge delocalization into the cyclopropyl group even in the "twisted" geometry of **1** raised the question of



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whether some delocalization is still possible in the unfavored 90°-twist geometry or whether the effect seen in **1** is to be attributed to the failure of the *o*-methyl substituents to constrain the cyclopropyl substituent to a perfect 90°-twist conformation.

We wish to report the results of solvolysis studies on the *p*-toluenesulfonate ester of 1-hydroxyadamantane-2-spirocyclopropane (**3c**) in which the cyclopropane ring is held rigidly in the twisted conformation. The results of acetolyses of tosylates **2c–5c** are shown in Table I.

Table I. Acetolyses of Adamantyl Tosylates at 45°

Tosylate	k, sec^{-1} [a]	k_{rel}	$\Delta H^{\pm}$, kcal/mol[b]	$\Delta S^{\pm}$, eu[b]
2c[c]	7.76×10^{-3}	1.1×10^4	20.3	−4.5
3c	5.03×10^{-5}	73	23.3	−5.0
4c	1.81×10^{-2}	2.6×10^4	19.0	−7.0
5c	8.0×10^{-7} [d]	1	26.7	−3.0

[a] With 0.02 *M* added $NaClO_4$. [b] Activation parameters determined over temperature ranges of from 25 to 40°. [c] P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961), report $k_{25°} = 5.86 \times 10^{-4}$ compared with our value, 5.15×10^{-4} sec^{-1}. [d] Extrapolated from data at higher temperatures.

In each case, unrearranged acetate is the predominant product.

Carbinol **6a**, mp 278–281° (sealed tube), was prepared in 38% yield by the magnesium sulfate buffered potassium permanganate oxidation[7] of 2-aminoadamantan-1-ol[8] in *t*-butyl alcohol–water solution at 25°. Treatment of **6a** with triphenylphosphine methylide in DMSO gave 33% of **5a**, mp 181–183° (sealed tube). Carbinol **3a**, mp 193–195° (sealed tube), was prepared in 83% yield by treating **5a** with the Simmons–Smith reagent.[9] Hydrogenolysis[10] of **3a** afforded **4a**, mp

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220–222° (sealed tube), in 96% yield. Tosylate **5c** was prepared by the treatment of the lithium salt of the corresponding alcohol with *p*-toluenesulfonyl chloride. Tosylates **2c–4c** were prepared by the conversion of the alcohols to the sulfinate esters[11] and oxidation by *m*-chloroperbenzoic acid[12] or ruthenium tetroxide.

The latter oxidation method, which can be applied at low temperature (<−20°) in nonpolar aprotic media (*i.e.*, halocarbon solvents), was particularly useful for the preparation of the more reactive tosylates **2c** and **4c**. This leads us to suggest the ruthenium tetroxide oxidation of sulfinate esters as a generally useful extension of the method of Coates and Chen[12] for the preparation of hindered or very reactive tosylates.

Samples of authentic acetates were prepared by treatment of the carbinols with ketene in chloroform containing a trace of sulfuric acid, characterized by nmr and ir spectroscopy, and compared with the reaction products by establishing identity using glpc–mass spectrometry.

The tremendous accelerations expected[1-6] for ionizations of cyclopropylcarbinyl or allyl tosylates are absent in **3c** and **5c**. Their acetolyses (45°) are actually *slower* than those of model compound **2c** (or **4c**) by *ca.* 10^2 and 10^4, respectively. Clearly the conjugative stabilization of a carbonium ion center by an adjacent perpendicular cyclopropyl ring or vinyl group is insignificantly small.

The deceleration seen for **3c** and **5c** could be attributed to (a) steric inhibition of solvation (shown to be unimportant by the fast acetolysis of **4c**, which has the even bulkier *gem*-dimethyl at C-2), (b) increased transition state angle strain for sp^2 hybridization at C-2 compared with the sp^3 hybridization of **2c** and **4c** (the angle at C-2 is compressed toward 90° in the cation), or (c) inductive transition-state destabilization by the more electronegative cyclopropyl or vinyl group at C-2. Explanation b may contribute to the difference between **3c** and **2c** but can hardly be significant in the comparison of **3c** and **5c**, both of which have essentially sp^2 hybridization at C-2. Explanation c is favored by the observation of a rough correlation of rates with the σ^* values[13] appropriate for the α substituents in **2c–5c**.

It is interesting to note that the 3-kcal/mol $\Delta\Delta H^{\pm}$ between **3c** and **5c** is of the same sign and approximate magnitude as the comparable difference seen[14] for model compounds lacking the geometric restraints of **3c** and **5c**. This suggests that the resonance stabilizations of planar allyl and bisected cyclopropylcarbinyl cations are nearly equal, despite calculations[15] (EHT) of a 3-kcal/mol larger barrier to rotation for cyclopropylcarbinyl than for allyl cation.

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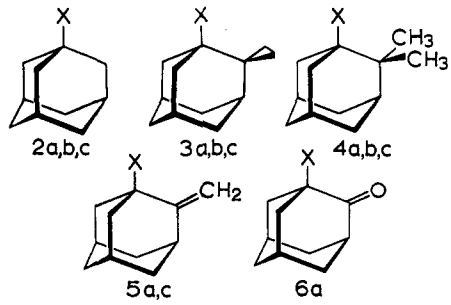

Figure 1. Compounds studied (**a**, X = OH; **b**, X = *p*-toluenesulfinyl; **c**, X = *p*-toluenesulfonyl).

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N-Methylacetohydroxamic Acid Catalyzed Ester Hydrolysis[1]

Sir:

Related to our efforts to develop intracomplex nucleophilic catalysts[2] for ester hydrolysis, it was essential to find intermolecular nucleophilic catalysts of high efficiency and relatively simple chemistry. An efficient nucleophilic catalyst for ester hydrolysis must combine the properties of high nucleophilicity toward ester substrates with exceptional lability of all intermediates on the pathway leading to the formation of products and regeneration of the catalyst.[3] Toward labile esters, the best nucleophiles known with pK_a's in the neutral pH range are functional groups exhibiting the α effect,[4] such as hydroxamate ion and hydroxylamine. However, the acyl intermediates formed by most such nucleophiles are either stable to hydrolysis or undergo decomposition reactions which do not regenerate the original nucleophile.[5] This is the case with hydroxamate ions since acylhydroxamates readily undergo the Lossen rearrangement to form isocyanates.[6] We sought to remedy this deficiency by alkyl substitution on the hydroxamic acid nitrogen, since with this modification the Lossen rearrangement cannot occur and deacylation must regenerate the hydroxamate ion. Furthermore, acyl derivatives of N-alkylhydroxamic acids are exceptionally labile in aqueous solution; for example, the hydrolysis rate of N,O-diacetyl-N-methylhydroxylamine is comparable to that of *p*-nitrophenyl acetate.[7]

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