# THE INFLUENCE OF DISTORTIONS IN THE SIGMA SKELETON
# ON THE STABILITY AND CHEMISTRY OF ALLYLIC CATIONS

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In connection with our investigation of pi-pi sigma-interactions during the solvolysis of allylic esters (1), we observed that the 3,5-dinitrobenzoate of 7-(2'-hydroxyethylidene)-norbornane (I) undergoes solvolysis in 70% aqueous acetone at a rate retarded by a factor of ca. 28 relative to that for 3,3-dimethylallyl 3,5-dinitrobenzoate (II, Table 1). Since both I and II are primary, $\gamma$,$\gamma$-dialkyl-substituted allylic esters, this retardation is unexpected. We now report the initial results of an investigation designed to test the possibility that this variance results from the relative destabilization of the transition state for ionization of I by distortions inherent in its sigma framework.

Ester I differs from II in that the endocyclic CCC angle in I is badly pinched, while the $CH_3$-C-$CH_3$ angle in II is normal. Since no rehybridization at this tertiary position accompanies ionization of I and II, to a first approximation one might expect this fact to have no influence on the relative free energy difference between ground and transition states for I and II. If, however, the in-plane bending force constants for cationic carbon are greater than for neutral $sp^2$-hydridized carbon, ionization of I would be accompanied by an angle strain increment not attendant upon solvolysis of II. Whereas little is known about bending force constants for positively charged carbon, the observation that radicals appear to be generated more readily than cations at identical strained bridgehead positions (2) suggests that at least the out-of-plane bending force constants for cationic carbon may exceed those for neutral carbon.

In order to test the hypothesis that bond angle distortion exerts a rate retarding influence on the solvolysis of I, esters III, IV, and V were synthesized and the kinetics and products of their solvolyses determined (Table 1). The hypothesis predicts a monatonic increase in rate for the series III<IV<V as the internal CCC angle at tertiary carbon becomes progressively less strained.

As predicted by the hypothesis, III, the compound for which the endocyclic tertiary CCC angle is most severely distorted, exhibits a solvolysis rate retarded relative to both IV and V. Two features of the data presented in Table 1 are unanticipated by the simple

bond angle distortion hypothesis, however. (i) The endocyclic tertiary CCC angle for IV is constricted while that for V is normal; hence one predicts $k_V > k_{IV}$, whereas the opposite order is observed experimentally. (ii) The bond angle distortion for III exceeds that for I, yet $k_{III}$ is greater than $k_I$ by a full order of magnitude.

Both of these apparent anomolies are explained if one postulates partial sigma-pi sigma delocalization of electron density from the 2,3-sigma bond to the developing allylic cation system during ionization of III (Figure 1) and IV (Figure 2). Such a postulate finds



Fig. 1                                                        Fig. 2
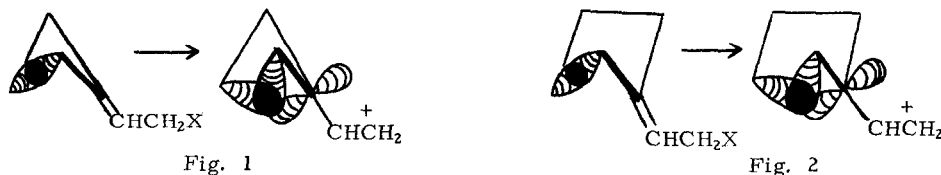
precedent both in the observation of comparable pi-pi sigma delocalization during solvolysis of VI, and in the calculated (3) and observed (4) delocalization of electron density from the 2,3-sigma bond to the developing cationic center during solvolysis of cyclobutyl derivatives. Since the cyclopentylidene ring in IV has available a conformation which allows the geometrical relationship of the 2,3-sigma-bond to the tertiary carbon to mimic that calculated to lead to sigma-electron delocalization in the cyclobutyl cation, an observable, though markedly diminished contribution of such delocalization to the stabilization of the transition state for solvolysis of IV does not appear unreasonable.*

The contribution of sigma delocalization to transition state stabilization would be expected to diminish sharply with the increase in ring size in the series III > IV > V. Since transition state destabilization due to bond angle distortion decreases in the same order, a peaking of reaction rate for IV as a consequence of the resolution of these competing effects is a plausible experimental result. Similarly, the contribution of sigma delocalization to the stabilization of the transition state for III could serve to counteract the adverse effect of greater bond angle distortion and thus account for the observation that $k_{III}$ exceeds $k_I$.

The cyclopentylidene ring in I is rigidly held in a conformation inappropriate for sigma delocalization to the allylic system. Conversely, derivatives of 2-(2'-hydroxyethylidene)-
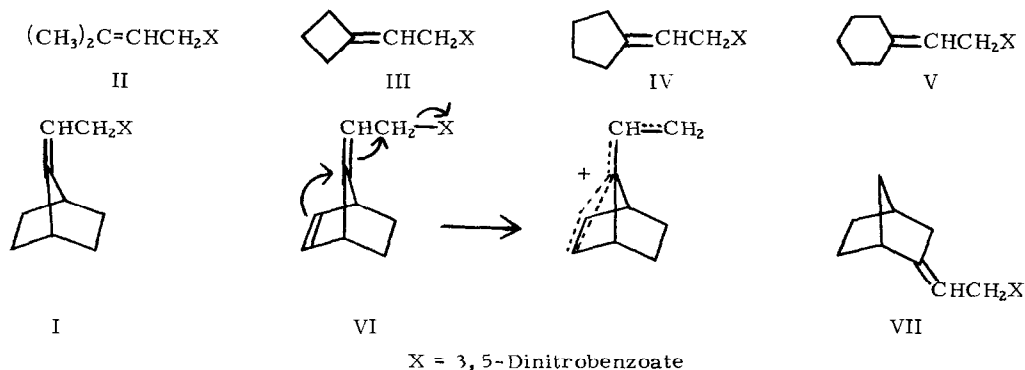
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*Sharp discontinuities are rarely encountered by the physical organic chemist. Since sigma delocalization during the generation of the cyclobutyl cation is well grounded in both theory and experiment (3, 4), it would be surprising if some such delocalization did not accompany generation of the cyclopentyl cation. The failure to observe direct evidence for such delocalization most likely results from the fact that the intrusion of two competing effects, generation of increased bond angle strain and relief of ground state torsional strain, renders impossible a precise prediction of the relative rates of solvolysis expected for cyclobutyl, cyclopentyl, and cyclohexyl derivatives in the absence of sigma delocalization.

norbornane (VII) possess a rigid framework which should optimize <u>sigma</u> delocalization to C-2 from both the C-1, C-6 and C-1, C-7 <u>sigma</u> bonds; significantly, the solvolysis of VII is accelerated relative to IV(5) despite an unfavorable constriction of the endocyclic bond angle at tertiary carbon.

Table 1. Kinetic Parameters and Products of Solvolysis of Allylic 3, 5-Dinitrobenzoates.

| Compound[a] | $k_{100°} \times 10^5$ (sec.$^{-1}$)[b] | $\Delta H^{\ddagger}$ (kcal./mole) | $\Delta S^{\ddagger}$ (e. u.) | Solvolysis Product Alcohols[b, c] % Primary(P) | % Tertiary(T) | T/P[d] |
|---|---|---|---|---|---|---|
| I | 0.337 | 27.3 | -11.0 | 70 | 30 | 0.43 (12) |
| I-T | 0.819 | 30.3 | -5.7 | 64 | 35 | 0.56 |
| III | 3.84 | 24.8 | -12.8 | 62 | 22 | 0.35 (57) |
| III-T | 2.59 | 27.0 | -7.7 | 31 | 19 | 0.61 |
| II | 9.38 | 24.9 | -10.8 | 14 | 35 | 2.5 |
| II-T | 229. | 23.2 | -8.8 | — | — | — |
| V | 9.15 | 26.3 | -7.1 | — | — | 3.4[e] |
| V-T | 122. | 26.5 | -1.4 | — | — | — |
| IV | 43.2 | 23.8 | -10.7 | 25 | 52 | 2.1 (0.3) |
| IV-T | 2350. | 23.4 | -3.8 | 15 | 33 | 2.2 |

(a) The suffix T denotes the tertiary allylic isomer of the numbered structure. (b) Solvolyses were conducted in 70% aqueous acetone in the presence of excess urea, a non-nucleophilic base added to sequester 3, 5-dinitrobenzoic acid as it is generated. (c) Yields are absolute and were determined by comparison of g. l. c. peak areas (suitably corrected for variations in molar response factor) to that of an internal standard, 1-decanol. Significant yields of olefinic products resulted from some solvolyses. (d) The equilibrium ratio (acid catalysis) is reported in parenthesis. (e) Only relative yields were determined.



$(CH_3)_2C=CHCH_2X$      =CHCH₂X      =CHCH₂X      =CHCH₂X

II      III      IV      V

CHCH₂X      CHCH₂—X      CH≡CH₂     

CHCH₂X

I      VI      VII

X = 3, 5-Dinitrobenzoate

A survey of the products generated by solvolysis of esters I-V (Table 1) also suggests that distortions within the sigma framework may significantly effect the chemistry of the intermediate allylic cation. The cations derived from I and III, in which the endocyclic tertiary angle is most severely strained, are unique among unsymmetrically disbustituted allylic cations in that they yield a preponderance of product derived from attack at the primary carbon. The observation that the normal kinetically controlled product of such unsymmetrically substituted allylic cations generated under limiting $S_N1$ conditions is primarily derived from attack at the tertiary position is generally rationalized by postulating a greater positive charge density at the more highly substituted terminus of the allylic cation (6). If, indeed, in plane bending force constants for $sp^2$ hybridized cationic carbon exceed those for $sp^2$ hybridized neutral carbon, one would expect a shift in pi-electron density from the primary to the tertiary carbon in the intermediates generated from I and III relative to the distribution which obtains in the unstrained allylic cation.

In summary, we believe that the data presented in Table 1 strongly support the hypothesis that resistance to bond angle deformation is greater at cationic carbon than at comparably hybridized neutral carbon. In addition, these data suggest that sigma-pi sigma delocalization from cyclobutane and cyclopentane sigma bonds contributes to the stabilization of incipient allylic cations generated from precursors possessing a geometry suitable for orbital overlap.

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