## Substituent Effects on Cyclopropylcarbinyl Solvolysis Rates. Evidence for Symmetrical Transition States

*Sir:*

The renowned conjugative interaction of cyclopropane rings with adjacent carbonium ions[1] continues to be demonstrated impressively. Cyclopropylcarbonium ions are unusually stable.[1-3] Cyclopropylcarbinyl derivatives solvolyze with markedly enhanced rates[1,4-10] to give rearranged and position scrambled products of the allylcarbinyl, cyclobutyl, and cyclopropylcarbinyl types.[1-14] There must be extensive charge delocalization from the carbinyl carbon of the cyclopropyl carbonium ion to the cyclopropane ring, but the nature and the extent of this delocalization is still not generally agreed upon.

Many structures for the cyclopropylcarbonium ion have been considered.[1-3,12,15-17] The classical representation, I,[1b] implies to us localization of the charge to the 1' position in a manner similar to that in the isobutyl or in the cyclohexylcarbinyl cation. We regard I as unsatisfactory in view of the abundant evidence for conjugation; some kind of "dotted line" formulation appears to us preferable. In certain cases the homoallylic cation, II, with charge distributed between C-1' and C-2, may be favored,[15,16] but this structure seems unlikely for simple cyclopropylcarbinyl systems.[1,15-17]

The "tricyclobutonium ion",[12] with $C_{3v}$ symmetry and essentially no charge on the methine group (C-1) (III), has received neither experimental[12] nor theoretical[15-17] support.



I    II    III    IV

V    VI    VII

$VIII^{1c}$    IX

Two different structures are favored by two schools of investigators: the unsymmetrical "bicyclobutonium ion" (IV-V),[6,8,12,17] and a symmetrical "bisected" form (VI-IX).[2,3,17] These two structures have different charge distribution. All four carbons bear charge in VI-IX, but IV and V predicts instantaneous delocalization only onto C-1', C-1, and C-2, *but not onto C-3*. In support of VI-IX analogies with cyclopropanecarboxaldehyde[17,18a] cyclopropyl methyl ketone,[18b] cyclopropanecarboxylic acid chloride,[18b] and phenylcyclopropane[19] are cited.[1c,2,3,17] These molecules prefer bisected conformations (like IX) which, presumably, permit maximum overlap of the p orbital of the carbon adjacent to the ring with the cyclopropane "bent bonds."[1]

We report here the simple approach to this problem of using methyl groups as probes for charge delocalization in the transition states of cyclopropylcarbinyl solvolyses (Table I). The rate enhancements produced by substitution of a single methyl group in various positions is summarized in XVIII. The effect of a second methyl group is shown in XIX and XX. The



XVIII    XIX

XX

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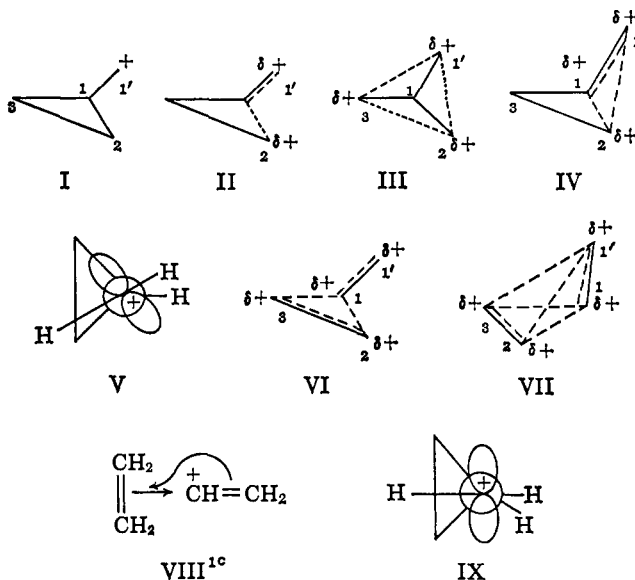
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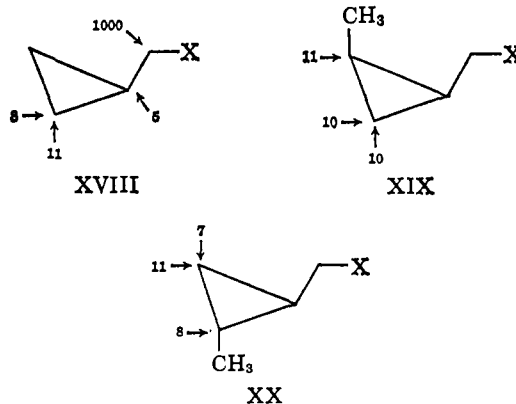(16) M. E. H. Howden and J. D. Roberts, *ibid.*, **2**, 403 (1963).

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**Table I.** First-Order Rate Data for Solvolysis of Cyclopropylcarbinyl 3,5-Dinitrobenzoates in 60% Aqueous Acetone at 100°

| Cyclopropylcarbinyl 3,5-dinitrobenzoate | | $k_1$, sec$^{-1}$ | Relative rates | | |
|---|---|---|---|---|---|
| | | | Obsd | Calcd[a] | Lit. |
| 1 | Parent | $4.30 \times 10^{-7}$ | 1.0 | 1.0 | 1.0 |
| 2 | 1-Methyl | $2.13 \times 10^{-6}$ | 5.0 | ... | 4.7[b],[c]4.8,[d] 5.5,[e] 50[f] |
| 3 | 1'-Methyl | $4.37 \times 10^{-4}$ | 1020 | ... | |
| 4 | trans-2-Methyl | $4.75 \times 10^{-6}$ | 11.0 | (11.0) | |
| 5 | cis-2-Methyl | $3.50 \times 10^{-6}$ | 8.2 | (8.2) | |
| 6 | 2,2-Dimethyl | $3.97 \times 10^{-5}$ | 92 | 90 | 96[b] |
| 7 | trans,tran.-2,3-Dimethyl | $5.33 \times 10^{-5}$ | 124 | 121 | |
| 8 | cis,cis-2,3-Dimethyl | $3.53 \times 10^{-5}$ | 82 | 67 | |
| 9 | cis,trans-2,3-Dimethyl | $3.45 \times 10^{-5}$ | 80 | 90 | |
| 10 | trans-2,3,3-Trimethyl | $2.12 \times 10^{-4}$ | 490 | 1000 | |
| 11 | 2,2,3,3-Tetramethyl | $6.75 \times 10^{-4}$ | 1570 | 8100 | |
| 12 | trans-2-Ethoxy | $4.03 \times 10^{-4}$ | 940 | ... | |
| | | Polycyclic Compounds | | | |
| 13 | X, $n = 8$ | $3.77 \times 10^{-5}$ | 88 | | |
| 14 | X, $n = 7$ | $2.20 \times 10^{-5}$ | 51 | | |
| 15 | X, $n = 6$ | $9.65 \times 10^{-5}$ | 220 | | |
| 16 | X, $n = 5$ | $1.70 \times 10^{-5}$ | 40 | | 36[g] |
| 17 | XI | $3.78 \times 10^{-6}$ | 8.8 | | |
| 18 | X, $n = 4$ | ... | ... | | 1.3[h] |
| 19 | XII | $4.00 \times 10^{-4}$ | 930 | | |
| 20 | XIII | $5.42 \times 10^{-4}$ | 1260 | | |
| 21 | XIV | $6.00 \times 10^{-6}$ | 14 | | |
| 22 | XV | $4.43 \times 10^{-5}$ | 103 | | |
| 23 | XVI-PNB[7] | $2.17 \times 10^{-6}$ [7] | | | 300[i] |
| 24 | XVII-PNB | | | | 1000[j] |

[a] Calcd by eq 1. [b] Methanesulfonates in 96% ethanol at 20°.[6b] [c] Tosylates in acetic acid at 25°.[5a] [d] p-Methoxybenzenesulfonates in acetic acid at 25°.[5a] [e] Benzenesulfonates in acetic acid at 25°.[5a] [f] Chlorides in 50% ethanol. Rough comparison; rate constants were not reported at the same temperature. This ratio seems suspect. [g] Tosylates in acetic acid with added KOAc at 25°.[4a] Comparison made with data for the parent compound in acetic acid alone.[5a] [h] Tosylates in acetic acid at 17°.[4b] [i] Comparison assuming p-nitrobenzoates solvolyze six times slower than 3,5-dinitrobenzoates. [j] p-Nitrobenzoates in 90% acetone at 118.6°.[4c]

2- and 3-methyl substituents have a remarkably constant multiplicative effect. Each additional group enhances the rate independent of the number and location of its neighbors; the factor for a trans-2 or 3-methyl (11.0) is slightly larger than the cis factor (8.2) (eq 1).

$$k_{\text{subst}}/k_{\text{parent}} = 8.2^{N_{cis\text{-}2 \text{ or } 3\text{-}CH_3}} \times 11.0^{N_{trans\text{-}2 \text{ or } 3\text{-}CH_3}} \quad (1)$$

I–IX differ in their prediction of the extent of charge delocalization. Our methyl results are clearly most consistent with symmetrical structures VI–IX for the



X, R=H
XII, R=CH₃

XI

XIII

XIV

XV

CH₂ODNB
XVI, $n = 5$
XVII, $n = 3$
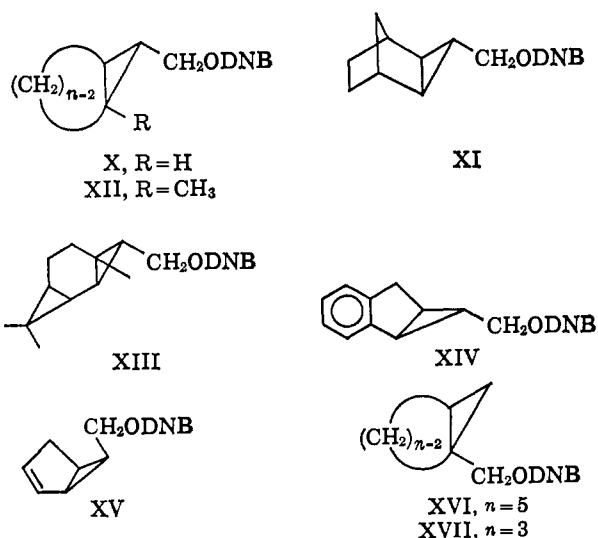
cyclopropylcarbinyl cation transition state and are not consistent with the bicyclobutonium formulations IV and V. An additional curious structural effect is easily

explicable on this basis: the unexpected *decrease* in rate in the series 15 → 18, with an *increase* in ring strain. Structures VI–IX predict a *shortening* of the C-2,3 bond in the ion. A small, strained ring attached to these positions would experience an increase of strain during ionization. Perhaps the small deviations of the relative rates of **10** (twofold) and of **11** (fivefold) from their calculated values (Table I) can be attributed to the same effect. Compounds **23** and **24** are *accelerated* by an increase of strain of the second ring due to the opportunity for C-1,2 bond lengthening in the transition state.

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## The Electronic Multiplicity of Thermally Generated Cyanonitrene. A Thermochemical "Heavy-Atom" Effect

*Sir:*

We have recently reported[1] that cyanonitrene (NCN) generated from thermal decomposition of cyanogen azide,[2] in the absence of a solvent, inserts[3] into the C–H

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