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THE ONE-ELECTRON REDUCTION OF CARBONIUM IONS. X.

CONFORMATIONAL EFFECTS OF CYCLOPROPYL GROUP ON THE RATE OF ONE-ELECTRON REDUCTION OF CYCLOPROPYLTROPYLIUM ION WITH CHROMOUS ION[1]

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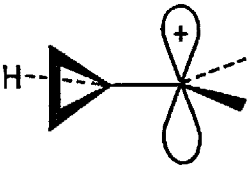
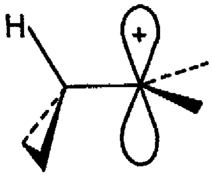
Abundant data have been accumulated to indicate that the electronic contribution of the cyclopropyl group to the carbonium-ion center occurs best from the bisected arrangement (I) and not from the parallel one (II).[2]

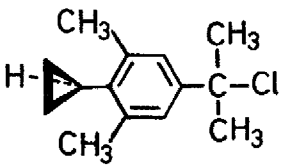


I

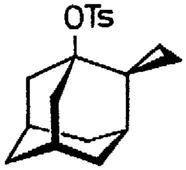


II

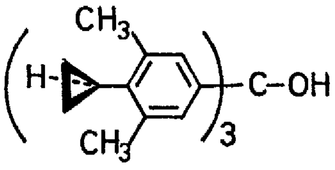
This has been successfully shown by the studies of the rates of solvolysis of III[3] and IV,[4] and the pK_R+ of the cation derived from V,[5] where the cyclopropyl groups are constrained to such geometries that cannot achieve the bisected arrangement in the stages of carbonium ions.



III



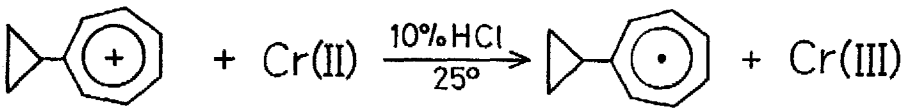
IV



V

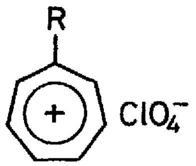
In the above works, however, such conformational effects examined were concerned with those of the cyclopropyl groups either located at a position distant from the carbonium-ion center across the benzene ring in the t-cumyl (III) and the trityl (V) systems, or fixed in the rigid parallel arrangement in the transient cation derived from IV.

In the course of our study of one-electron reduction of various substituted tropylium ions,[6] we were interested to see the conformational effects of the cyclopropyl group as a substituent on the stability of the tropylium ion, as estimated from the rates of the one-electron reduction (eq. 1), because the tropylium system was thought to be unique in that the electronic contribution of the cyclopropyl group is directly transmitted to the carbonium carbon, and moreover, the conformation is easily controlled by introducing flanking methyl groups to the tropylium ring.

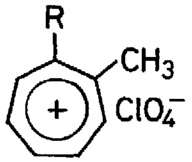


(1)

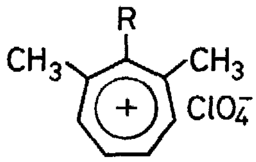
If the cyclopropyl group of the bisected arrangement (I) most effectively stabilized the tropylium ion, the introduction of one or two methyl groups flanking the cyclopropyl group would make the cyclopropyl group difficult to attain the bisected conformation and to result in destabilization of the tropylium ion. Meanwhile, it has previously been observed that a linear correlation holds between the cation stability (pK_{R^+}) and the reduction rate ($\log k_2$).[16b) Therefore, such a destabilizing effect was expected to cause acceleration of the reaction, provided the electronic effects of the methyl groups were properly corrected. Consequently, we synthesized various alkyltropylium perchlorates (VI - VIII) and determined their rates of one-electron reduction with chromous ion in 10% hydrochloric acid at 25°. The perchlorates were prepared from the corresponding alkyltropilidenes[8) in the usual manner[9) and the second-order rate constants determined by the method previously reported.[16a) The results are summarized in Table 1.



VIa,[7a) VIb, VIc[7a,b)



VIIa, VIIb, VIIc



VIIIa, VIIIb, VIIIc

a: R = H b: R = CH_3 c: R = cyclo-Pr

Table 1. The Second-order Rate Constants for the One-electron Reduction of Various Substituted Tropylium Ions with Chromous Ion in 10% Hydrochloric Acid at 25°. [Tropylium ion]$_0$= 2.3-3.1x10^{-3} g-ion·l^{-1}; [Cr(II)]$_0$=8.0-12x10^{-3} g-ion·l^{-1}

Tropylium perchlorate[a]	VIa[d]	VIb	VIc[d,e]	VIIb[f]	VIIc[g]	VIIIa[h]	VIIIb[i]	VIIIc[j]
k_2,[b] l·g-ion^{-1} sec^{-1}	74.0 ±0.2[c]	11.1 ±0.2[c]	4.62 ±0.08	0.908 ±0.010	0.929 ±0.09	2.33 ±0.06	0.148 ±0.002	0.335 ±0.004

a) All new compounds gave spectral and microanalytical data consistent with the proposed structure. b) Averaged value from three runs. c) Ref. 16b. d) Fluoroborate. e) Mp 58.2-60.0°. f) Mp 106.0-107.5°. Reported value is 97-99° (ref. 17). g) Mp 90.6-91.6°. h) Mp 78.0-80.0°. i) Mp 167.5-168.3°. j) Mp 146.0-146.4°.

The conformational effects of the cyclopropyl group on the rates of one-electron reduction are visualized by the plot of the log k_2 values for the two series of compounds, VIIa-c and

VIIIa-c, against those for the corresponding VIa-c.[10] Evidently no linear free-energy relationship holds in both of VIIc and VIIIc,[11,12] indicating the destabilization of the tropylium ions, VIIc and VIIIc. The results are most reasonably explained on the basis that the cyclopropyl group of VIc can assume a bisected conformation, while that of VIIc and VIIIc is constrained by the flanking methyl groups to conformations rather close to the parallel geometry.[13]

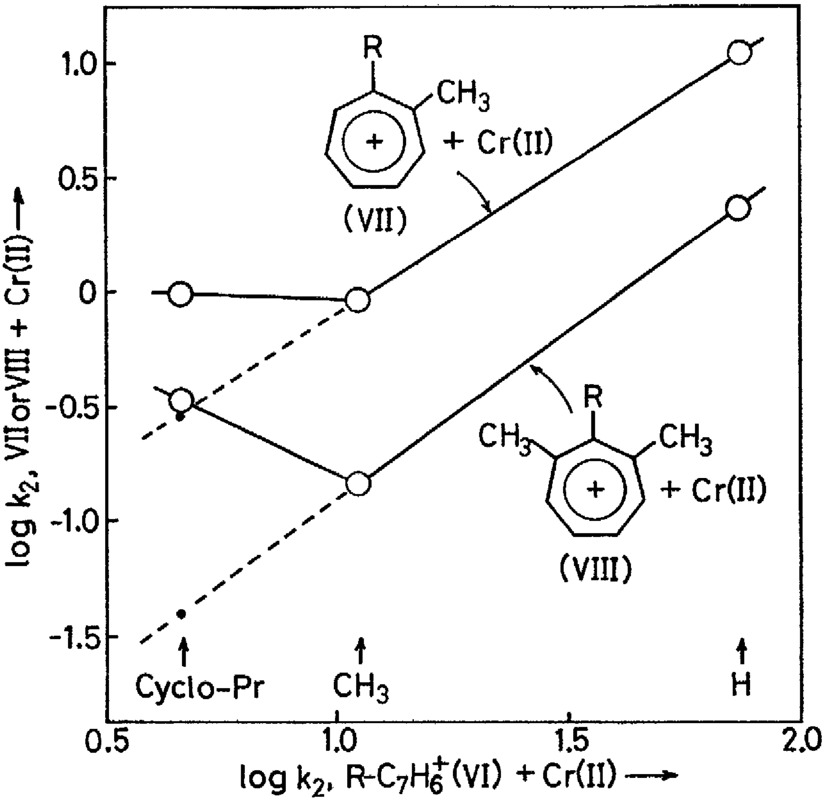


Fig. 1. Relationship between log k_2 values for VII or VIII and those for VI in the one-electron reduction with chromous ion in 10% hydrochloric acid at 25°.

It is worth pointing out that the rate constants for VIIc and VIIIc are greater than those predicted assuming a linear correlations in Fig. 1 by factors of 3.3 and 8.0, respectively. On the other hand, in the p-cyclopropyl-t-cumyl system, the introduction of a single methyl group ortho to the cyclopropyl group decreases the rate of solvolysis by a corrected factor of 2, while the introduction of two methyl groups decreases it by a corrected factor of 18.[3] The contrast between the two systems with respect to the effectiveness of a single methyl group (3.3/8.0 vs. 2/18) suggests that the cyclopropyl group of the tropylium ring is more susceptible to the steric effect of a single flanking methyl group as compared with that of the phenyl ring. Presumably, the cyclopropyl group in VIIc is twisted away from the bisected conformation more than that in the p-cyclopropyl-m-methyl-t-cumyl cation owing to the greater steric repulsion between the methyl and the methine hydrogen of the cyclopropyl group as compared with the case of the t-cumyl system.[18]

References and notes

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2) For detailed reviews, see: a) H. G. Richey, Jr., in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, 1972, Chapter 25; b) K. B. Wiberg, H. A. Hess, Jr., and A. J. Ashe, III, in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, 1972, Chapter 26.
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7) a) The fluoroborate was used instead of the perchlorate. b) The preparation of the fluoroborate has been reported, but no melting point described in the literature (N. L. Bauld, J. D. McDermed, C. E. Hudson, Y. S. Rim, J. Zoeller, Jr., R. D. Gordon, and J. S. Hyde, J. Am. Chem. Soc., 91, 6666 (1969)).
8) A new route to various alkyltropilidenes has been explored for the present work. K. Takeuchi, K. Yasuda, and K. Okamoto, Chem. Lett., 715 (1976).
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10) Attempts to determine the pK_{R^+}'s failed for most of VI, VII, and VIII owing to their instability in aqueous ethanol. Therefore, the correlation of log k_2 with pK_{R^+} could not be examined.
11) The plot of log k_2 for VIa-c against the σ^+-values[14,15] gives a straight line with ρ^+ +2.61 (correlation coefficient 0.9997, standard deviation along the ordinate 0.024). Therefore, electronic contribution of the cyclopropyl group in the reaction (eq. 1) is believed to be much greater to the cation than to the produced radical.
12) The log k_2 values have been successfully correlated with C. T. energy (ν_{max}) for monosubstituted tropylium ions.[6] In the present work, however, di- and tri-substituted tropylium ions showed ν_{max} values ($2.10\text{-}2.11 \times 10^{-4} cm^{-1}$) similar to each other, with pyrene as the standard electron donor. This appears to suggest the leveling of electron delocalization from the alkyl groups to the tropylium ring in the C. T. complex formation, and the research along this line is underway.
13) The ^1H NMR spectra of VIc, VIIc, and VIIIc also suggest that the delocalization of the positive charge to the cyclopropyl group decreases in this order.
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18) An examination of molecular models supports this postulate.