There was no sign of any induced decomposition at the temperature of our experiments and the concentration of **1** and **2** under steady illumination had the required dependence on the light intensity.[7-11]

Results and Discussion

The data used to derive $k_i/2k_t$ are listed in Table I. These results come from three separate experiments, in each of which the temperature was changed in a random manner. A least-squares treatment of these data gives the Arrhenius equation

$$\log(k_i/2k_t/\mathrm{M}) = (0.57 \pm 0.71) - (3.69 \pm 0.45)/\theta$$

where the errors are standard deviations and θ is $2.3RT$ kcal/mol.

The data used to derive $2k_t$ are listed in Table II. Radical **2** was generated by photolysis of *tert*-butyl cyclopropylperacetate in methylcyclopropane at temperatures where only **2** was present in detectable concentrations. Least-squares treatment of these data gives

$$\log(2k_t/\mathrm{M}^{-1}\,\mathrm{s}^{-1}) = (11.91 \pm 0.15) - (2.25 \pm 0.12)/\theta$$

Since the solvent and reactant are identical in the two sets of experiments the Arrhenius equations can be combined. This gives

$$\log(k_i/\mathrm{s}^{-1}) = (12.48 \pm 0.85) - (5.94 \pm 0.57)/\theta$$

which yields

$$k_i = 1.3 \times 10^8\ \mathrm{M}^{-1}\,\mathrm{s}^{-1} \text{ at } 25\ °\mathrm{C}$$

in satisfactory agreement with our earlier estimates.[5] The pre-exponential factor is within the expected range,[14] though a value closer to $10^{13.0}$ s^{-1} seems more likely to be correct,[15] in which case the rate constant for isomerization at room temperature would be about 2×10^8 M^{-1} s^{-1}.

The present results and our earlier data on the isomerization of other primary, nonstabilized,[16,17] alkyl radicals are collected, for convenience, into Table III. The wide range in the rates of isomerization of the radicals in this table illustrate both the utility and the versatility of our EPR spectroscopic techniques. We hope that our data on these isomerizations will provide useful standards for future kinetic investigations.

References and Notes

(1) Issued as N.R.C.C. No. 15537. Part 26. G. Brunton, D. Griller, L. R. C. Barclay, and K. U. Ingold, *J. Am. Chem. Soc.*, earlier paper in this issue.

(2) (a) NATO Fellow 1974–1975; (b) N.R.C.C. Research Associate 1975–1976.

(3) J. W. Wilt in "Free Radicals", Vol. 1, J. K. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 8.

(4) S. J. Cristol and R. V. Barbour, *J. Am. Chem. Soc.*, **90**, 2832 (1968).

(5) D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **90**, 7047 (1968).

(6) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Am. Chem. Soc.*, **91**, 1877 (1969); see also: *ibid.*, **91**, 1879 (1969).

(7) D. Griller and B. P. Roberts, *Chem. Commun.*, 1035 (1971); *J. Chem. Soc., Perkin Trans. 2*, 747 (1972).

(8) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 993 (1972).

(9) G. B. Watts, D. Griller, and K. U. Ingold, *J. Am. Chem. Soc.*, **94**, 8784 (1972).

(10) D. Lal, D. Griller, S. Husband, and K. U. Ingold, *J. Am. Chem. Soc.*, **96**, 6355 (1974).

(11) B. Maillard and K. U. Ingold, *J. Am. Chem. Soc.*, **98**, 1224 (1976).

(12) R. A. Sheldon and J. K. Kochi, *J. Am. Chem. Soc.*, **92**, 4395 (1970).

(13) R. A. Sheldon and J. K. Kochi, *J. Am. Chem. Soc.*, **92**, 5175 (1970).

(14) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968.

(15) The loss in entropy in the transition state due to the loss of rotational freedom about the cyclopropyl-$\dot{\mathrm{C}}\mathrm{H}_2$ bond will be approximately compensated for by the fourfold degeneracy of the reaction (cf. ref 14).

(16) D. Griller and K. U. Ingold, *Acc. Chem. Res.*, **9**, 13 (1976).

(17) Of the radicals listed in Table III only 1 is stabilized and its stabilization energy is only 0.4 ± 1.6 kcal/mol.[18]

(18) D. F. McMillen, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kinet.*, **3**, 359 (1971).

3-Tricyclo[3.2.1.0^{2,7}]octyl (3-Homonortricyclyl) Cations. Steric Criteria in Degenerate Cyclopropylcarbinyl Rearrangements and the Classical vs. Nonclassical Nature of Cyclopropylcarbinyl Cations[1]

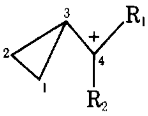
George A. Olah* and Gao Liang

Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.

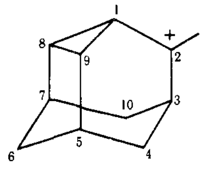
Received July 22, 1975

Abstract: The 3-tricyclo[3.2.1.0^{2,7}]octyl (3-homonortricyclyl) cations (**5**-H, -CH$_3$, and -Br) generated from different precursors under stable ion conditions underwent degenerate cyclopropylcarbinyl rearrangement, shown by their temperature-dependent proton and carbon-13 NMR spectra studied between −85 and 20 °C. The tertiary 3-chloro-3-tricyclo[3.2.1.0^{2,7}]octyl cation **5**-Cl was shown to be static and did not undergo cyclopropylcarbinyl rearrangement. Ion **5**-H was unexpectedly also formed from the allylic 2-bicyclo[3.2.1]oct-3-enyl cation (**12**). The mechanism of rearrangement of **12** into **5**-H is discussed. Based on both carbon-13 and proton chemical shifts and one-bond coupling constants ($J_{\mathrm{C-H}}$) in a series of cyclopropylcarbinyl type cations, the classical vs. nonclassical nature of cyclopropylcarbinyl cations (**1**) is discussed.

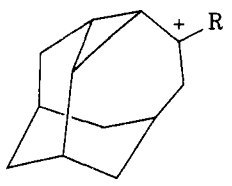
The structure of cyclopropylcarbinyl cations has received much attention[2] and has also been subjected to theoretical treatments.[3] While all experimental evidence supports the static carbenium ion nature of long lived secondary and tertiary cyclopropylcarbinyl cations[4,5] (with varying degrees of charge delocalization into the cyclopropyl ring), the parent, primary cyclopropylcarbinyl cation undergoes rapid degenerate rearrangement. The facile degenerate cyclopropylcarbinyl–cyclopropylcarbinyl rearrangement taking place in the parent primary ion **1** ($R_1 = R_2 = H$) is absent when replacing hy-



1



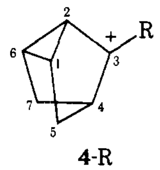
2



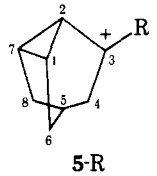
3

drogen with methyl groups at the carbenium center (R_1 = CH_3, R_2 = H or CH_3), i.e., in secondary and tertiary systems. We recently have also found that the secondary 8,9-dehydro-2-adamantyl cation (**2**, R = H) is undergoing rapid degenerate equilibrium under stable ion conditions.[6] The cyclopropylcarbinyl-cyclopropylcarbinyl type rearrangement is, however, blocked when substituting hydrogen with methyl, i.e, in the tertiary ion **2** (R = CH_3).

We have further found that the secondary-secondary cyclopropylcarbinyl rearrangement can only be slowed down (at the NMR time scale at −120 °C) in the parent 2,4-dehydro-5-homoadamantyl cation (**3**, R = H), but it is completely absent when substituting hydrogen with a methyl or phenyl group at C(5) (**3**, R = CH_3 or C_6H_5).[7] The high energy barrier for degenerate cyclopropylcarbinyl rearrangements is also reflected by the direct observation of the secondary and tertiary 3-nortricyclyl cations (**4**, R = H, CH_3, and C_6H_5) as static carbenium ions with charge delocalization into the cyclopropane ring.[8]

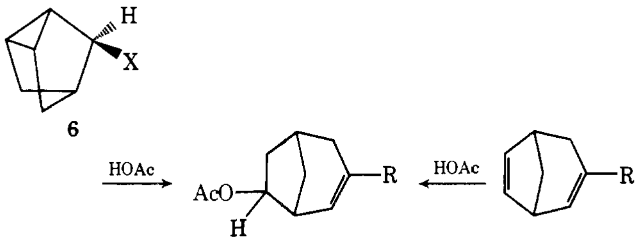


4-R



5-R

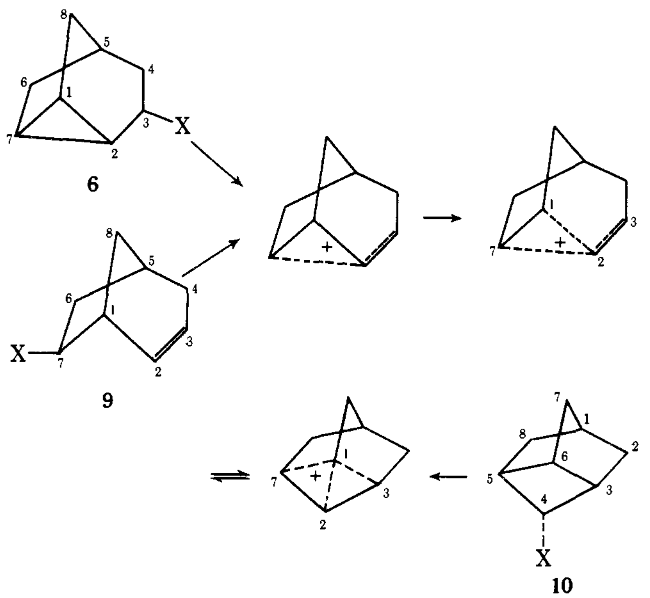
A natural extension of the study of 3-nortricyclyl cations would be that of 3-homonortricyclyl cations,[9] i.e., 3-tricyclo[3.2.1.0^{2,7}]octyl cations (**5**). These ions are also cyclopropylcarbinyl-type cations allowing the preferred bisected geometry for conjugation with the cyclopropane ring. Sauer, Beisler, and Feilich[10] reported that the acetolysis of the *p*-nitrobenzoate **6**-OPNB gave only the acetate of the unsaturated alcohol **7** (R = H), which was also formed upon the addition of acetic acid to bicyclo[3.2.1]octa-2,6-diene (**8**-H).



6

7 (R = H) **8**-H (R = H)

These reactions thus must involve ion **5** as intermediate. Ion **5** was also suggested by LeBel[11] and Berson[12] to be involved in the solvolysis of a series of bicyclooctenyl and tricyclooctyl derivatives. More recently, Grob et al.[13] suggested ion **5** as the intermediate in the solvolytic cyclopropylcarbinyl-cyclobutyl-homoallyl rearrangement of tricyclo[3.2.1.0^{2,7}]octan-3-ol (**6**, X = OPNB), *exo*-bicyclo[3.2.1]oct-2-en-7-ol (**9**, X = OPNB), and *endo*-tricyclo[3.2.1.0^{3,6}]octan-4-ol (**10**, X = OPNB). In formic or trifluoroacetic acid, deuterium label in positions 1, 3, or 7 is completely scrambled.[14] To explain the data in more nucleophilic media (e.g., 70% aqueous dioxane) the symmetrical, bisected cation is only needed. The study is thus very similar to that reported by Baldwin and Foglesong in the solvolysis of 8,9-dehydro-2-adamantyl derivatives.[15,30]

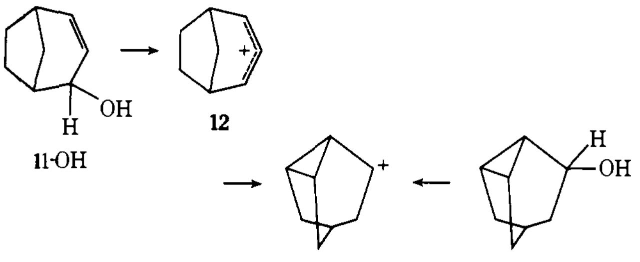


6 **9** **10**

In continuation of our preceding studies, we now wish to report the preparation and NMR spectroscopic study of the 3-tricyclo[3.2.1.0^{2,7}]octyl (or 3-homonortricyclyl) cation (**5**), its formation from the 2-bicyclo[3.2.1]oct-3-enyl cation (**12**), as well as the investigation of the degenerate cyclopropylcarbinyl rearrangement of the ion.

Results and Discussion

Preparation of the 3-Homonortricyclyl Cation and its ^{1}H and ^{13}C NMR Study. The 2-bicyclo[3.2.1]oct-3-enyl cation (**12**) was generated from its alcoholic precursor **11**[16b,17] in SbF_5-SO_2ClF solution at dry ice-acetone temperature (ca. −78 °C). The high symmetry of **12** is clearly indicated in its proton and carbon-13 NMR spectra (Figure 1).[18] NMR parameters and assignments of **12** at −85 °C are summarized in Table I. When compared with the cyclopentenyl (**13**) and cyclohexenyl (**14**) cations,[19] ion **12** is best described as a typical bicyclic allylic cation.



11-OH **12** **5-H** **6-OH**

13

14

When **12** was slowly warmed to 20 °C, the ^{1}H NMR spectrum of the ion showed the irreversible formation of a new carbocation (Figure 2). The ^{1}H NMR spectrum of this new ion once formed shows reversible temperature-dependent behavior between −100 and 20 °C. The same cation **5**-H also was obtained from tricyclic alcohol **6**-OH[13] under identical conditions. At temperatures below −95 °C the ^{1}H NMR spectrum of **5**-H (Figure 1b) shows deshielded broad one-proton signals at δ 3.38 and a four-proton AB quartet centered at δ 2.45. The ^{13}C NMR spectrum of the same solution at −85 °C (Figure 3) allowed the structural assignment of the new species as the tricyclyl [3.2.1.0^{2,7}]octyl-3-yl cation (**5**-H).

The temperature-dependent ^{1}H NMR spectra of ion **5**-H show that as the temperature is raised to 20 °C:[20] (a) the sig-

Table I. Proton and Carbon-13 NMR Parameters of Bicyclo[3.2.1]oct-3-en-2-yl and Tricyclo[3.2.1.$0^{2,7}$]oct-3-yl Cations[a]

Ion		T, °C	1	2	3	4	5	6	7	8
5-H	$\delta_{^1\mathrm{H}}$	−85	5.84 (b)	5.08 (b)	10.44 (b)	3.38	3.38	2.45	5.84	2.45
		20	7.32 (d-h, 6.2, 1.5)	5.05 (q, 6.2)	7.32 (d-d, 6.2, 1.5)	2.82 (q, 1.5)	3.44 (b)	2.82 (q, 1.5)	7.32 (d-d, 6.2, 1.5)	2.82 (q, 1.5)
	$\delta_{^{13}\mathrm{C}}$	−85	85.64 (d, 175.7)	81.26 (d, 192.7)	234.12 (d, 168.1)	43.62 (t, 129.8)	31.56 (d, 152.1)	31.56 (t, 137.0)	85.64 (d, 175.7)	31.56 (t, 137.0)
		20	(135.8)	82.28	(135.18)	36.19	32.47	36.19	(135.18)	36.19
5-CH_3[b]	$\delta_{^1\mathrm{H}}$	−85	4.98 (d, 5.8)	4.30 (t, 5.8)		3.18 (s)	3.00 (b)	exo 1.80 (d, 13.6) endo 2.50 (d-d, 13.6, 4.2)	4.98	exo 1.80 endo 2.50
	$\delta_{^{13}\mathrm{C}}$	−85	72.6 (d, 183.6)	70.8 (d, 192.0)	260.5 (s)	46.9 (t, 130.0)	29.7 (d, 149.2)	30.7 (d-d, 136.3, 138.6)	72.6	30.7
5-Br	$\delta_{^1\mathrm{H}}$	−85	4.2 (m)	4.2 (m)		3.14 (s)	3.10 (b)	exo 2.04 (d, 14.8) endo 2.54 (d-d, 14.8, 4.0)	4.2	exo 2.04 endo 2.54
	$\delta_{^{13}\mathrm{C}}$	−85	81.5 (d, 189.8)	81.5 (d, 189.8)	229.8 (s)	51.9 (t, 132.1)	32.9 (d, 149.5)	31.4 (d-d, 137.7, 138.2)	81.5	31.4
5-Cl	$\delta_{^1\mathrm{H}}$	−60	5.39 (d, 5.6)	4.78 (t, 5.6)		3.28 (s)	3.22 (m)	exo 2.16 (d, 14.2) endo 2.72 (d-d, 14.2, 4.2)	5.39 (d, 5.6)	exo 2.16 (d, 14.2) endo 2.72 (d-d, 14.2, 4.2)
	$\delta_{^{13}\mathrm{C}}$	−60	79.13 (d, 187.5)	76.94 (d, 194.9)	234.01 (s)	48.91 (t, 133.8)	31.23 (d, 149.2)	31.49 (t, 136.8)	79.13 (d, 187.5)	31.49 (t, 136.8)
12	$\delta_{^1\mathrm{H}}$	−85	4.70 (b)	10.22 (d-d, 7.8, 7.0)	8.24 (t, 7.8)	10.22 (d-d, 7.8, 7.0)	4.70 (b)	exo 3.38 (b) endo 1.48 (d)		syn 2.24 anti 1.94
	$\delta_{^{13}\mathrm{C}}$	−85	50.50 (d, 153.7)	212.54 (d, 163.4)	136.10 (d, 177.8)	212.54 (d, 163.4)	50.50 (d, 153.7)	19.41 (t, 144.0)	19.41	40.43 (t, 144.0)

[a] Proton and carbon-13 chemical shifts are in parts per million from external Me_4Si (capillary). Multiplicities and coupling constants (J_{C-H} in hertz) are in parentheses; b = broad, d = doublet, m= multiplet, d-d = doublet of doublets, d-h = doublet of heptets, q = quartet, t = triplet. [b] CH_3: $\delta_{^1\mathrm{H}}$ 2.95 (s); $\delta_{^{13}\mathrm{C}}$ 32.8 (q, 130.8).

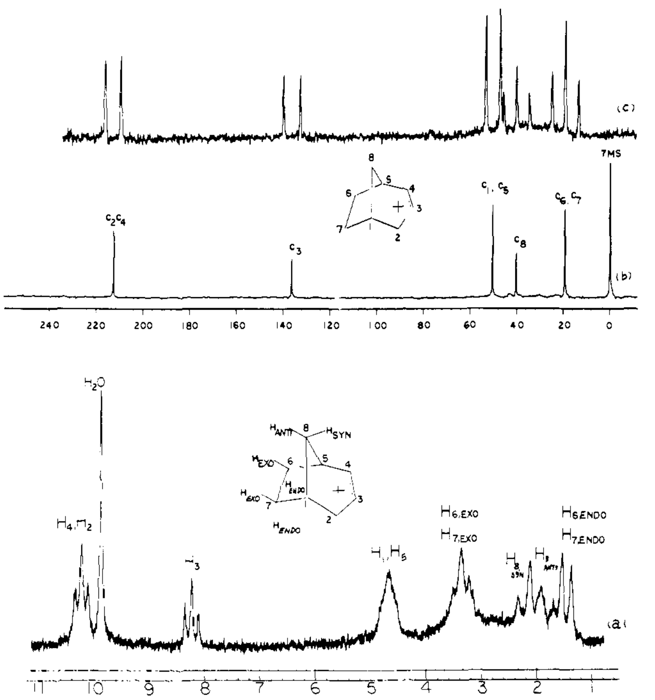
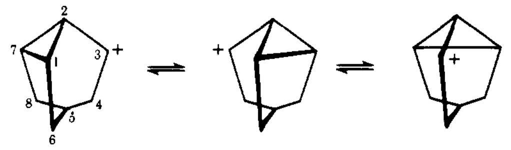


Figure 1. (a) ^1H NMR (60 MHz) spectrum of ion **12** in SbF_5-SO_2ClF solution at −85 °C. (b) ^{13}C proton noise decoupled NMR spectrum of ion **12**. (c) ^{13}C proton coupled NMR spectrum of ion **12**.

nals that are present in **5**-H at −85 °C at δ 10.44 and 5.84 become equilibrated to give a three-proton doublet of heptets centered at δ 7.32 (δ_{av} calcd = ⅓(10.44 + (2 × 5.84) = 7.37); (b) the one-proton signal at δ 5.08 becomes a quartet centered at δ 5.05; (c) the broad signal at δ 3.38 and the AB quartet become equilibrated to give a six-proton quartet centered at δ 2.82 (δ_{av} calcd = ⅙[(2 × 3.38) + (4 × 2.45)] = 2.76); and (d) the one-proton signal centered at δ 3.38 remains almost unchanged.

The temperature-dependent behavior of ion **5**-H was further studied by Fourier transform ^{13}C NMR spectroscopy. At −85 °C six carbon resonances are observed in ion **5**-H. As the temperature was slowly raised, signals due to C(3), C(1) and C(7), C(4) and C(6) and C(8) became broadened, while those due to C(2) and C(5) remained sharp. At 20 °C when the degenerate process became fast on the NMR time scale, carbon resonances due to C(1), C(3), and C(7) merged into the base line, those due to C(4), C(6), and C(8) merged into one signal and appeared at $\delta_{^{13}C}$ 36.19 ($\delta_{^{13}C_{calcd}}$ = ⅓(43.62 + (2 × 31.56)) = 35.58), while those due to C(2) and C(5) remain unchanged. Both the temperature-dependent proton and carbon-13 NMR spectra suggest that ion **5**-H undergoes an equilibration process which we attribute to the degenerate cyclopropyl carbinyl rearrangement as shown below.



Although the symmetrical 2-bicyclo[3.2.1]oct-3-enyl(**12**) was shown to be involved in the solvolytic reactions of bicyclooctenyl derivatives,[11-13,17] no evidence was given either for the formation of tricyclic products **6** or the transformation of **12** into **5**-H. Apparently the nucleophilic solvent captures **12** before rearrangement takes place. Under long-lived ion conditions, the transformation of **12** into **5**-H is considered to take place in the manner shown in Scheme I.

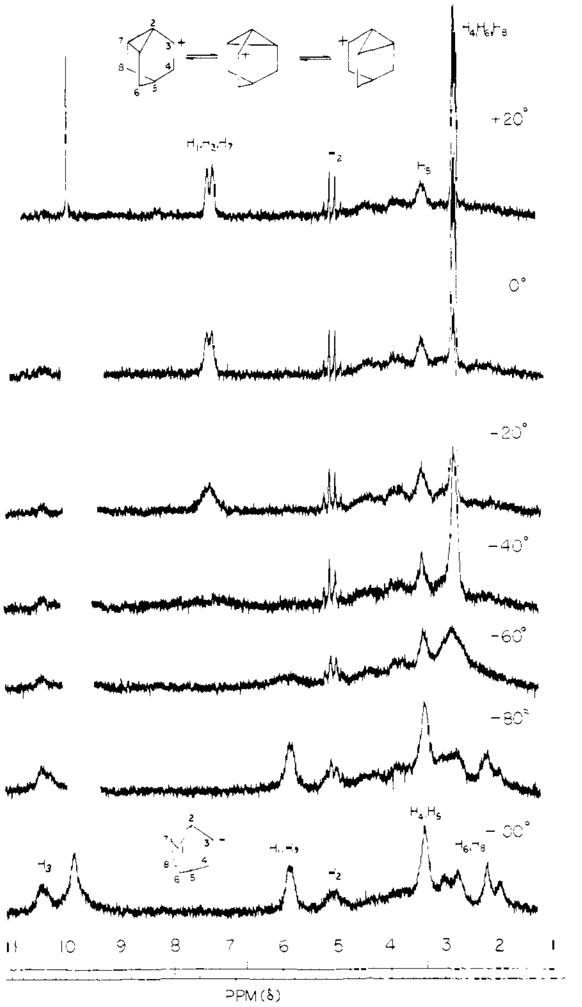


Figure 2. Temperature-dependent proton NMR spectra of ion **5**-H in SbF_5-SO_2ClF solution.

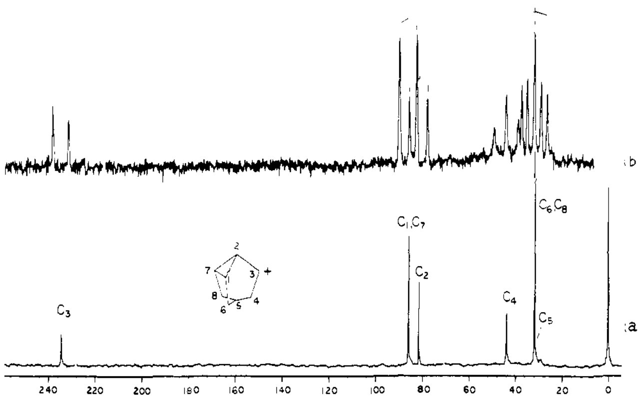


Figure 3. ^{13}C NMR spectra of ion **5**-H (a) proton noise decoupled: (b) proton coupled.

In principle, the 2-bicyclo[3.2.1]oct-3-enyl cation (**12**) might undergo facile 1,3-hydride shift[10,21] (process I) or Wagner–Meerwein rearrangement (processes II or III). If process I takes place, the 3-homonortricyclyl cation would be the product, while process II (or III) would give the isomeric 6-homonortricyclyl cation (**18**). Both ^1H and ^{13}C NMR spectra show that the ion formed is symmetrical. Therefore **5**-H is the rearranged product from **12**. In contrast, solvolytic studies indicate the opposite direction, e.g., products formed via **12** being isomeric with **18**.[22]

In order to further confirm the structure of the 3-homonortricyclyl cation (**5**-H) and the mechanism of the rear-

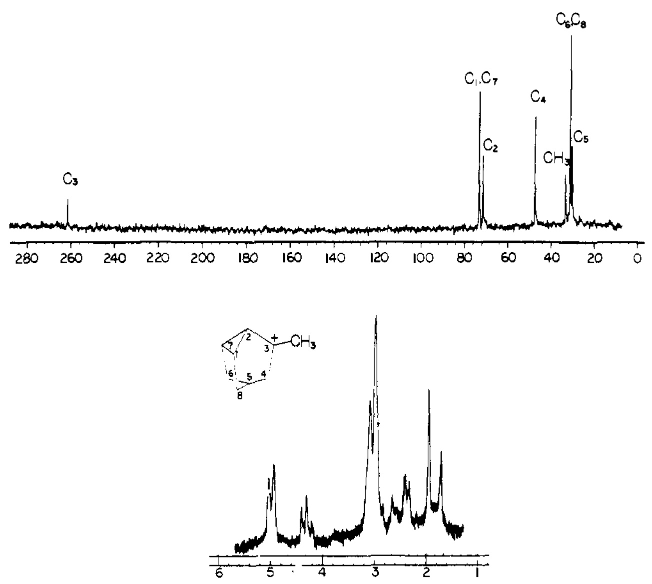


Figure 4. ^1H NMR (bottom trace) and ^{13}C NMR (proton noise decoupled) spectra of 3-methyl-3-homonortricyclyl cation (**5**-CH_3) in FSO_3H-SO_2ClF solution at −85 °C.

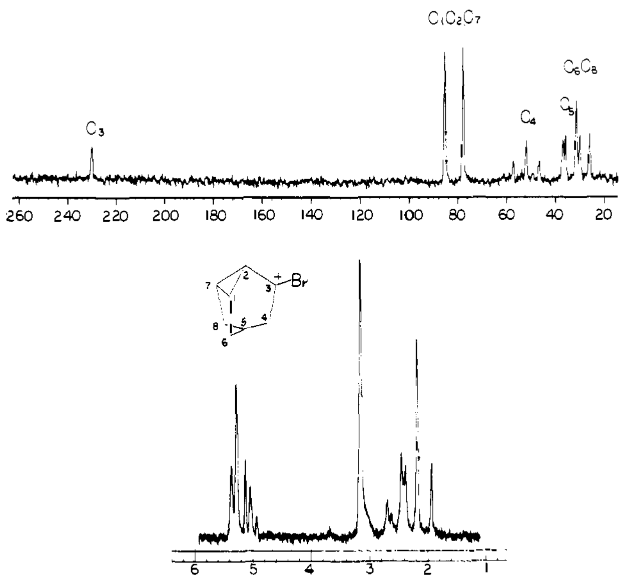


Figure 5. ^1H (60 MHz, bottom trace) and ^{13}C (proton coupled) NMR spectra of 3-bromo-3-homonortricyclyl cation in FSO_3H-SO_2ClF solution at −85 °.

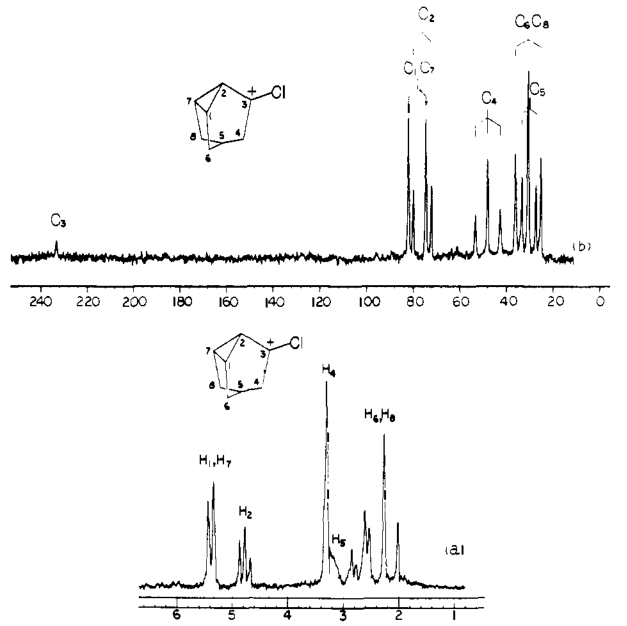
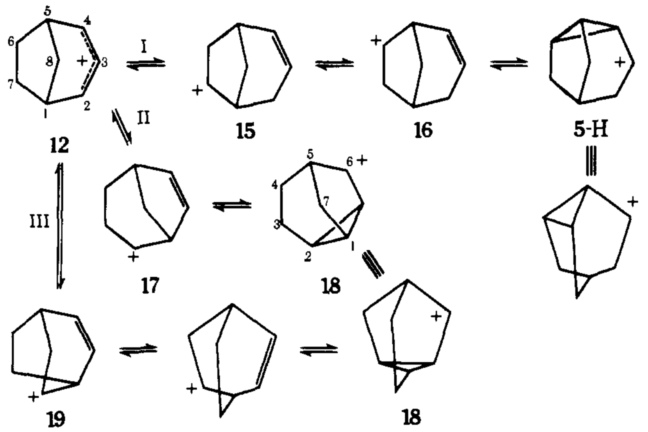
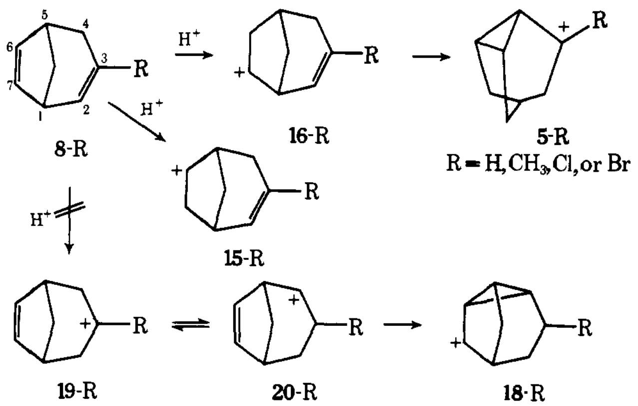


Figure 6. (a) Proton NMR spectrum of ion **5**-Cl in FSO_3H-SO_2ClF solution at −60 °C. (b) Proton coupled ^{13}C NMR spectrum.

Scheme 1

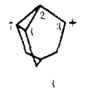
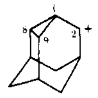
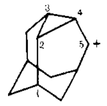
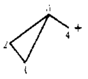




rangement of bicyclo[3.2.1]oct3-en-2-yl cation (**12**) to **5**-H, we were able to show that protonation of bicyclo[3.2.1]octa-2,6-dienes (**8**-R, R = H, CH_3, Cl, and Br) also give their corresponding 3-homonortricyclyl cations (**5**-R). When the parent diene (**8**-H)[23] 3-methyl-(**8**-CH_3), 3-chloro-(**8**-Cl), and 3-bromo-(**8**-Br) bicyclo [3.2.1]octa-2,6-dienes were treated with FSO_3H-SO_2 ClF solution at −78 °C, the corresponding 3-homonortricyclyl cations (**5**-R) were cleanly formed (Figures 4–6). The structural assignments of these ions are further confirmed by their ^{13}C NMR spectra (spectroscopic data are summarized in Table I with assignments). Both ^1H and ^{13}C NMR spectroscopic data indicate the symmetrical nature of the observed 3-homonortricyclyl cations (**5**-R) and thus excludes the formation of the unsymmetrical 6-homonortricyclyl cations (**18**-R). The protonation of dienes **8**-R taking place at C(6) instead of C(8), in the present acid system is thus in agreement with the previously reported acetic acid addition **8**.[10,22]

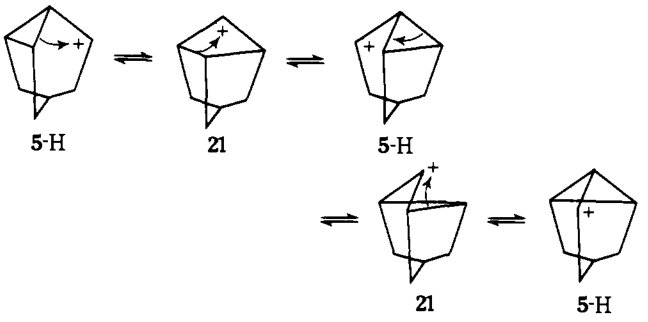
Steric Hinderance in Degenerate Cyclopropylcarbinyl Equilibration Process. In view of our studies it seems that the energy barrier for degenerate cyclopropylcarbinyl rearrangements is very sensitive to whether the cyclopropane ring can achieve proper spacial alignment with the neighboring carbocation center.[2-4,25] While we were unable to freeze out on the NMR time scale in the case of the parent cyclopropylcarbinyl cation (**1**, $R_1 = R_2 = H$) the primary–primary or in the case of the parent 8,9-dehydro-2-adamantyl cation (**2**-H) the secondary–secondary cyclopropylcarbinyl-cyclopropyl-

Table II

		δ ¹H			δ ¹³C		
			Equilibrium			Equilibrium	
Compd	Position	Static	Exptl	Calcd	Static	Exptl	Calcd
	1,7 3	5.85 10.44	7.32	7.37	85.64 234.12		$^1/_3((2 \times 85.64) + 234.12) = 135.2$
	8,9 2	6.0, calcd 10.5, calcd	7.96	7.5		157.0	
	2 5	6.94 10.64	8.78	8.79	127.83 239.25		$^1/_2(127.83 + 239.25) = 183.6$
	1,2 4	6.5, calcd 11.0, calcd	6.50	8.0	65.0, calcd 220.0, calcd	57.0	$^1/_3((2 \times 65) + 220) = 117.0$

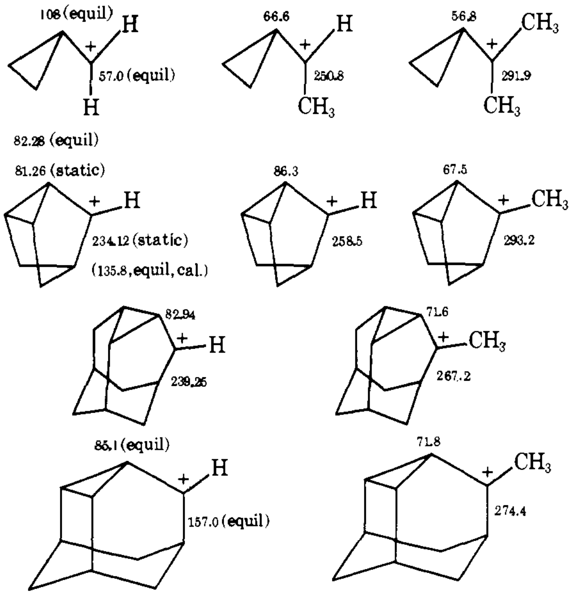
carbinyl rearrangement, the barrier for such processes in either a geometrically rigid system, i.e., the 3-homonortricyclyl cation (**5**-H), or a slightly distorted system, i.e., the 2,4-dehydro-5-homoadamantyl cation (**3**-H),[7] is much higher. In the even more rigid system, i.e., the 3-nortricyclyl cation (**4**-H),[8] the degenerate rearrangement is absent.

Quantum mechanical calculations seem to agree that the puckered cyclobutyl cation is involved in the degenerate cyclopropylcarbinyl rearrangement.[3] The fact that such processes take place at a lower temperature range in **3**-H (−120 to −60 °C) than in **5**-H (−85 to 20 °C) thus seems to indicate the reactive formation of the puckered cyclobutyl cation intermediate in the former.[2c] The geometrically more constrained system would make the formation of a cyclobutyl cation energetically less favorable, and thus make the cyclopropylcarbinyl rearrangement less feasible.[3m,r,26] Similarly as we have suggested in the case of 8,9-dehydro-2-adamantyl[6] and 2,4-dehydro-5-homoadamantyl[7] cations, the degenerate equilibration process taking place in the 3-homonortricyclyl cation (**5**-H) can be best explained by the following scheme going through cyclobutyl cation (**21**).



Question of the Classical vs. Nonclassical Ion Nature of Cyclopropylcarbinyl Cations. Since the term "nonclassical" cyclopropylcarbinyl cation was first used by Roberts and Mazur[27] to describe the nature of the intermediate carbocation involved in the reactions of primary cyclopropylcarbinyl derivatives, much debate concerning the classical vs. nonclassical nature of these ions took place.[2,5,28] Whereas the facile cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement was originally observed only in the parent ion **1** ($R_1 = R_2 = H$), it was since also attained, as discussed earlier, in more rigid secondary ions. Temperature-dependent ¹H and ¹³C NMR spectra for the secondary carbenium ions in both their static or equilibrating states are summarized in Table II. The calculated shifts for the series of secondary ions as equilibrating species are consistent with the experimental values. However, when using classical carbenium ions as models (with usual correction of replacing a CH_3 group with H) to calculate the primary ion **1**, the inconsistency is immediately seen. Although as explained we do not have experimental chemical shifts for comparison, extrapolation of values from the classical secondary and tertiary ions can be made. Methyl substitution generally causes an about 30-ppm deshielding effect at the carbenium ion center next to a cyclopropyl ring. Carbon shift of the carbenium ion center of the tertiary ion **1** ($R_1 = R_2 = CH_3$) is $\delta_{^{13}C}$ 281.9 and that of the secondary ion **1** (R_1 = H, $R_2 = CH_3$) is $\delta_{^{13}C}$ 250.8. A similar trend is also seen in several other series of carbocations for methyl substituent effects at the carbenium ion centers. We can thus estimate that the shift for the carbocationic center in the static primary ion **1** would be about $\delta_{^{13}C}$ 220, while that of the β-cyclopropane ring carbons (C(1) and C(2)) would be about $\delta_{^{13}C}$ 65. The average shift for the equilibrating classical ion thus would be $\frac{1}{3}[(2 \times 65) + 220)] = 117$. The observed shift $\delta_{^{13}C}$ 57.0 is, however, 60 ppm less shielded. Furthermore, the apical carbon (C(3)) in the parent cyclopropylcarbinyl cation resonates at $\delta_{^{13}C}$ 108, which is about 40–50 ppm more deshielded than those in either secondary or tertiary cyclopropylcarbinyl ions. The difference in carbon shifts for the apical carbons between secondary and tertiary cyclopropylcarbinyl cations is only about 10–20 ppm

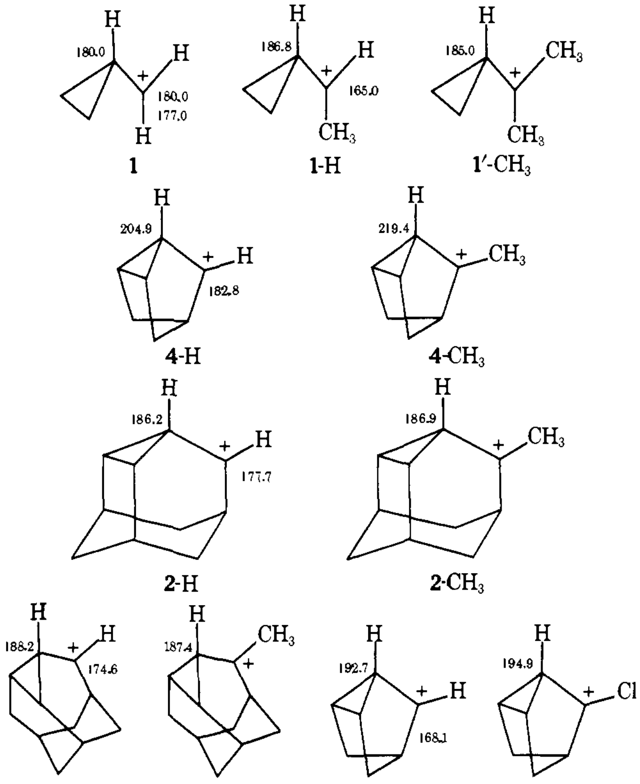
Scheme II



(see Scheme II). Apparently the observed shift for the apical cyclopropane carbon in the primary ion is unusually deshielded. It is clear that the apical carbon shifts in static cyclopropylcarbinyl-type ions should not be much different from those in the degenerate ions, as seen in the cases of 8,9-dehydro-2-adamantyl, 3-homonortricyclyl, and 2,4-dehydro-5-homoadamantyl cations. This is, however, clearly not the case for the primary cyclopropylcarbinyl cation (**1**).

One-bond $^{13}C-^{1}H$ coupling constants (J_{C-H}, in hertz) are known to increase markedly with increasing s character of the carbon hybridization,[29] although charge, substituent effects, and/or other factors are also considered to be contributors. We have listed J_{C-H} for the apical cyclopropane carbons in a series of cyclopropylcarbinyl-type cations for comparison (Scheme III). The value of J_{C-H} for apical cyclopropane carbons apparently increases with ring strain, going from the mobile cyclopropylcarbinyl cation (**1**)[8] to more rigid 8,9-dehydro-2-adamantyl (**2**)[6] and 2,4-dehydro-5-homoadamantyl (**3**)[7] cations, and to even more rigid 3-nortricyclyl (**4**)[8] and 3-homonortricyclyl (**5**). The coupling constants observed for the methylene group in **1** is, however, larger than those in all other static or equilibrating secondary ions (**2**-H, **3**-H, **4**-H, and **5**-H). They are also much larger than the methine coupling (J_{C-H} = 165.0) in the secondary ion **1**-H. The increase in the $^{13}C-^{1}H$ coupling constant is therefore consistent with the postulated increase in ring strain accompanying the formation of the σ bridge. The $^{13}C-^{1}H$ coupling constant for the apical cyclopropane ring carbon in **1**-H probably would not change much, although we do not know the exact geometry of the ion.

Scheme III



Kelly and Brown[30] recently criticized our conclusion relating to the structure of the parent cyclopropylcarbinyl cation (**1**) and claimed that the J_{C-H} value to 180 Hz for the apical CH group would support an equilibrating classical ion. It is clear from the foregoing discussion that one cannot differentiate classical or nonclassical character from this parameter. It is indeed surprising to see that they attribute to us criteria to "decide" the question of nonclassicality, based on a single value of J_{C-H} i.e., of the apical methine group, which incidentally is not participating in the overall equilibration process. In any case couplings are affected by many factors and their theory is quite complex. We know of no treatment which allows a quantitative evaluation of J_{C-H} either in carbocations or their neutral precursors, at the present time in cyclopropylcarbinyl systems. Our views on the nonclassical carbonium ion nature of the cyclopropylcarbinyl cation remain unchanged.

Experimental Section

Materials. Bicyclo[3.2.1]oct-3-en-2-ol (**11**),[16b,17] tricyclo[3.2.1.$0^{2,7}$]octan-3-ol(**6**-OH),[15] bicyclo[3.2.1]octa-2,6-diene(**8**-H)[23] 3-bromobicyclo[3.2.1]octa-2,6-diene(**8**-Br),[24] and 3-chlorobicyclo[3.2.1]octa-2,6-diene (**8**-Cl)[24] were prepared as previously described in literature.

3-Methylbicyclo[3.2.1]octa-2,6-diene(**8**-CH_3) was prepared by stirring **8**-Cl or **8**-Br in dry ether with excess of methyl magnesium iodide at room temperature for two days: bp 34 °C (0.2 mm); ^{1}H NMR ($CDCl_3$, capillary Me_4Si) δ 1.95 (s, 3 H), 2.0–2.9 (m, 6 H), 3.16 (m, 2 H), 6.18 (d-d, 2 H), and 6.64 (d-d, 1 H).

Preparation of Ions. A freshly prepared FSO_3H or SbF_5 solution in SO_2ClF (w/w) was cooled at dry ice-acetone bath temperature (ca. −78 °C). Into the acid solution was then slowly introduced with vigorous stirring a cold solution of bicyclic or tricyclic precursors in SO_2ClF to give an approximately 15–20% solution of the ion, which was then immediately transferred into a precooled NMR tube for study.

Proton and Carbon-13 NMR Spectroscopy. ^{1}H and ^{13}C NMR spectra were obtained using Varian Associates Models A56/60A and XL-100-15 NMR spectrometers, respectively. Both proton and carbon-13 shifts were measured from the external tetramethylsilane (capillary) signal. Details of the CFT spectroscopic conditions used were as described previously.[31]

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

References and Notes

(1) Stable Carbocations 196. Part 195. G. A. Olah, D. A. Forsyth, and R. J. Spear, *J. Am. Chem. Soc.*, in press.

(2) For recent reviews, see: (a) R. Breslow, *Mol. Rearrangements*, 1, 259 (1963); (b) P. D. Bartlett, "Nonclassical Ions", W. A. Benjamin, New York, N.Y., 1965; (c) K. B. Wiberg, in "Carbonium Ions", Vol. III, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1972; (d) N. C. Deno, *Prog. Phys. Org. Chem.*, **2**, 129 (1964); (e) H. G. Richey, Jr., in ref. 2b; (f) M. Hanack and H. J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967); (g) J. Haywood-Farmer, *Chem. Rev.*, **74**, 315 (1974); (h) S. Winstein, *Experientia, Suppl. II*, 137 (1955); (i) B. Capon, *Q. Rev., Chem. Soc.*, **18**, 45 (1964); (j) N. L. Wendler, *Mol. Rearrangements*, **2**, 1075 (1963); (k) M. Y. Lukina, *Russ. Chem. Rev.*, **32**, 635 (1963); (l) G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, **12**, 173 (1973); *J. Am. Chem. Soc.*, **94**, 808 (1972); (m) L. N. Ferguson in "Highlights of Alicyclic Chemistry", Franklin, Palisades, N.J., 1973.

(3) (a) H. Andrist, *J. Chem. Soc., Chem. Commun.*, 446 (1975); *J. Am. Chem. Soc.*, **95**, 753 (1973); (b) J. E. Wolf, P. G. Harch, R. W. Taft, and W. J. Hehre, *ibid.*, **97**, 2902 (1975); (c) W. J. Hehre and P. C. Hiberty, *ibid.*, **96**, 302 (1974); **94**, 5917 (1972); (d) W. J. Hehre, *ibid.*, **96**, 5207 (1974); (e) P. C. Hariharan, L. Radom, J. A. Pople, and P. v. R. Schleyer, *ibid.*, **96**, 600 (1974); (f) C. F. Wilcox, L. M. Loew, and R. Hoffmann, *ibid.*, **95**, 8192 (1973); (g) T. D. Goldman, *Tetrahedron*, **28**, 3175 (1972); (h) C. U. Pittman, Jr., C. Dyan, C. Engelman, and L. D. Kispert, *J. Am. Chem. Soc.*, **93**, 6948 (1971); (i) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); *Tetrahedron Lett.*, **43**, 3819 (1965); (j) L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 5935 (1972); (k) W. C. Danen, *ibid.*, **94**, 4835 (1972); (l) V. Buss, R. Gleiter, and P. v. R. Schleyer, *ibid.*, **93**, 3927 (1971); (m) K. B. Wiberg and G. Szeimies, *ibid.*, **92**, 571 (1970); **90**, 4195 (1968); (n) H. Kollmar and H. O. Smith, *Tetrahedron Lett.*, 3133 (1970); (o) J. E. Baldwin and W. D. Fogleson, *J. Am. Chem. Soc.*, **90**, 4311 (1968); (p) H. S. Tremper and D. D. Shillady, *ibid.*, **91**, 6341 (1969); (q) C. Trindle and O. Sinanoglu, *ibid.*, **91**, 4054 (1969); (r) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968); (s) R. E. Davis and A. Ohno, *ibid.*, **24**, 2063 (1968); (t) M. E. H. Howden and J. D. Roberts, *ibid.*, **19**, 403 (1963).

(4) (a) P. G. Gassman and W. C. Pike, *J. Am. Chem. Soc.*, **97**, 1250 (1975); (b) H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952); (c) K. L. Servis and J. D. Roberts, *ibid.*, **86**, 3773 (1964); **87**, 1331 (1965); (d) H. Hart and P. A. Law, *ibid.*, **86**, 1957 (1964); (e) H. Kim and W. D. Gwinn, *Tetrahedron Lett.*, 2535 (1964); (f) M. Hanack, S. Kang, J. Haffner, and K. Gorler, *Justus Liebigs Ann. Chem.*, **690**, 98 (1965); (g) C. C. Lee and I. S. Bhardwaj, *Can. J. Chem.*, **41**, 1031 (1963); (h) P. v. R. Schleyer and G. W. van Dine, *J. Am. Chem. Soc.*, **88**, 2321 (1966); (i) M. Hanack and H. Meyer, *Justus Liebigs Ann. Chem.*, **20**, 81 (1968); (j) I. Lillian and L. Handloser, *J. Org. Chem.*, **34**, 3058 (1969); (k) B. R. Ree and J. C. Martin, *J. Am. Chem. Soc.*, **92**, 1660

(1970); **91**, 5882 (1969), and references quoted therein; (l) M. J. S. Dewar and J. M. Harris, *ibid.*, **92**, 6557 (1970); (m) T. Shono, I. Nishiguchi, and R. Oda, *J. Org. Chem.*, **35**, 42 (1970); (n) J. E. Rhodes and V. G. DiFate, *J. Am. Chem. Soc.*, **94**, 7582 (1972); (o) Z. Majerski and P. v. R. Schleyer, *ibid.*, **93**, 665 (1971); (p) R. G. Ghirardelli, *ibid.*, **95**, 4987 (1973); (q) C. D. Poulter and C. J. Spillner, *ibid.*, **96**, 7591 (1974); (r) D. G. Garratt, A. Modro, K. Oyama, G. H. Schmid, T. T. Tidwell, and K. Yates, *ibid.*, **96**, 5295 (1974); (s) D. F. Eaton and T. G. Graylor, *ibid.*, **96**, 1226 (1974).

(5) (a) H. Volz, J. H. Shin, and H. J. Streicher, *Tetrahedron Lett.*, 1297 (1975); (b) G. A. Olah, C. L. Jeuell, D. P. Kelley, and R. D. Porter, *J. Am. Chem. Soc.*, **94**, 146 (1972); **92**, 2544 (1970); (*c*) G. A. Olah and P. W. Westerman and J. Nishimura, *ibid.*, **96**, 3548 (1974); (e) D. S. Kabakoff and E. Namanworth, *ibid.*, **92**, 3234 (1970); (f) A. Brown and G. H. Schmid, *Can. J. Chem.*, **50**, 2432 (1972); (g) G. A. Olah and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **87**, 5123 (1965); (h) H. G. Richey, Jr. and J. M. Richey, *ibid.*, **88**, 4971 (1966), and references quoted therein.

(6) G. A. Olah, G. Liang, R. K. Murray, Jr., and K. A. Babiak, *J. Am. Chem. Soc.*, **96**, 6794 (1974).

(7) G. A. Olah, G. Liang, R. K. Murray, Jr., and K. A. Babiak, *J. Am. Chem. Soc.*, **98**, 576 (1976).

(8) (a) G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **95**, 3792 (1973); *ibid.*, **97**, 1920 (1975).

(9) The name "homonortricyclyl" is used for 3-tricyclo[3.2.1.0^{2,7}]octyl system as its relationship to the previously reported 3-nortricyclyl system.

(10) (a) R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967); (b) R. R. Sauers and J. A. Beisler, *Tetrahedron Lett.*, 2181 (1964).

(11) N. A. LeBel, R. A. Greengard, M. T. Tribble, J. H. Siefert, and R. D. Bach, *J. Am. Chem. Soc.*, **95**, 8182 (1973).

(12) (a) J. A. Berson, *Angew. Chem., Int. Ed. Engl.*, 7, 779 (1968); (b) J. A. Berson, J. M. McKenna, and H. Junge, *J. Am. Chem. Soc.*, **93**, 1296 (1971); (c) J. A. Berson and J. W. Foley, *ibid.*, **93**, 1297 (1971); (d) J. A. Berson, D. Wege, G. M. Clarke, and R. G. Gergman, *ibid.*, **91**, 5594 5601 (1969); **90**, 3236, 3238, 3240 (1968).

(13) C. A. Grob, M. Geisel, W. Santi, and W. Tschudi, *Helv. Chim. Acta*, **56**, 1046, 1055 (1973); *Tetrahedron Lett.*, 4311 (1972).

(14) C. A. Grob, private communication.

(15) J. E. Baldwin and W. D. Foglesong, *J. Am. Chem. Soc.*, **90**, 4303 (1968); **89**, 6372 (1967).

(16) (a) H. L. Goering and M. F. Sloan, *J. Am. Chem. Soc.*, **83**, 1992 (1961); (b) H. L. Goering, R. W. Greiner, and M. F. Sloan, *ibid.*, **83**, 1391 (1961); (c) H. L. Goering and D. L. Towns, *ibid.*, **85**, 2295 (1963).

(17) (a) K. Alder, H. Krieger, and H. Weiss, *Chem. Ber.*, **88**, 144 (1955); (b) R. R. Sauers, *Tetrahedron Lett.*, 146 (1961); (c) K. B. Wilberg and G. R. Wenzinger, *J. Org. Chem.*, **30**, 2278 (1965).

(18) (a) The ^{1}H NMR spectrum of ion **12** was previously reported, see A. F. Diaz, D. L. Harris, M. Sakai, and S. Winstein, *Tetrahedron Lett.*, 303 (1971); (b) Detail NMR analysis of a series of bicyclo[3.2.1]oct-3-enyl cations will be reported subsequently.

(19) (a) G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **94**, 6434 (1972); **97**, 1987 (1975); (b) G. A. Olah, G. Liang, and Y. K. Mo, *ibid.*, **94**, 3544 (1972).

(20) The ion slowly decomposed at higher temperature.

(21) For the existence of 1,3-hydride shifts see: M. Saunders, P. Vogel, E. L. Hagen, and J. Rosenfield, *Acc. Chem. Res.*, **6**, 53 (1973).

(22) (a) R. K. Bly and R. S. Bly, *J. Org. Chem.*, **31**, 1577 (1966); (b) G. N. Gickes, *ibid.*, **34**, 1513 (1969); (c) M. A. Battiste, J. M. Coxon, and R. Edelman, *Tetrahedron Lett.*, 4577 (1972); (d) N. A. LeBel and R. J. Maxwell, *J. Am. Chem. Soc.*, **91**, 2307 (1969); (e) N. A. LeBel, J. E. Huber, and L. H. Zalkow, *ibid.*, **84**, 2226 (1962); (f) W. C. Widlman and D. R. Saunders, *ibid.*, **76**, 946 (1954); (g) J. W. Wilt and D. R. Sullivan, *J. Org. Chem.*, **40**, 1036 (1975); (h) G. W. Klumpp, J. W. F. K. Barnick, A. H. Veefkind, and F. Bickelhaupt, *Recl. Trav. Chem. Pays-Bas*, **88**, 766 (1969).

(23) (a) J. M. Brown, *J. Chem. Soc. B*, 730 (1971); (b) J. M. Brown and J. L. Occolowitz, *ibid.*, 411 (1968); *Chem. Commun.*, 376 (1965); (c) C. Cupas, W. E. Watts, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **86**, 2503 (1964).

(24) R. C. De Selms and C. M. Combs, *J. Org. Chem.*, **28**, 2206 (1963).

(25) (a) L. M. Stock and P. E. Young, *J. Am. Chem. Soc.*, **94**, 4247 (1972); (b) H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *J. Org. Chem.*, **31**, 295 (1966); (*c*) M. Pelissier, A. Serafini, J. Davanneaux, J-F. Labarre, and J-F., Tocanne, *Tetrahedron*, **27**, 3271 (1971); (d) J. V. Paukstelis and J-L. Kao, *Tetrahedron Lett.*, 3691 (1970); (e) P. v. R. Schleyer and V. Buss, *J. Am. Chem. Soc.*, **91**, 5880 (1969); (f) H. C. Brown and J. D. Cleveland, *ibid.*, **88**, 2051 (1966); (g) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949); (h) G. L. Closs and H. B. Klinger, *J. Am. Chem. Soc.*, **87**, 3265 (1965).

(26) (a) K. B. Wiberg and G. Szeimies, *J. Am. Chem. Soc.*, **92**, 571 (1970); (b) K. B. Wiberg and T. Nakahira, *Tetrahedron Lett.*, 3759 (1970); (c) K. B. Wiberg and R. Genoglio, *ibid.*, 1273 (1963); (d) K. B. Wiberg, J. E. Hiatt, and K. Hseih, *J. Am. Chem. Soc.*, **92**, 544 (1970); (e) K. B. Wiberg and J. G. Pfeiffer, *ibid.*, **92**, 553 (1970); (f) K. B. Wiberg, V. Z. Williams, Jr., and L. E. Friedrich, *ibid.*, **92**, 564 (1970); (g) K. B. Wiberg, R. A. Fenoglio, V. Z. Williams, Jr., and R. W. Ubersax, *ibid.*, **92**, 568 (1970); (h) R. J. Piccolini and S. Winstein, *Tetrahedron*, **19**, 423 (1963); (i) C. D. Poulter and S. Winstein, *J. Am. Chem. Soc.*, **91**, 3650 (1969).

(27) J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 3542 (1951).

(28) (a) H. C. Brown in "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972, Chapter 9; (b) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Siver, and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959); (c) M. Vogel and J. D. Roberts, *ibid.*, **88**, 2262 (1966); (d) W. Huckel, *J. Prakt. Chem.*, **28**, 27 (1965); (e) A. Jensen, *Tidsskr. Kjeml. Bergves., Metall.*, **28**, 98 (1968); (f) P. D. Bartlett, *Justus Liebigs Ann. Chem.*, **653**, 45 (1962); (g) H. C. Brown, *Chem. Soc., Spec. Publ.*, **No. 16**, 154 (1962).

(29) (a) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **91**, 5801 (1969); (b) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972; (c) D. G. Farnum, *Adv. Phys. Org. Chem.*, 11, 123 (1975).

(30) D. P. Kelly and H. C. Brown, *J. Am. Chem. Soc.*, **97**, 3897 (1975).

(31) G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **96**, 189 (1974).

Cytochrome *c* Peroxidase Catalyzed Oxidations of Substitution Inert Iron(II) Complexes

W. L. Purcell and James E. Erman*

Contribution from the Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115.

Received March 29, 1976

Abstract: The kinetics of the reduction of compound II of cytochrome *c* peroxidase as a function of temperature have been determined for a variety of iron(II) reductants of varying redox potential. A linear free-energy relationship has been obtained between free-energy changes for the reactions and the activation free energies consistent with the Marcus theory for outer-sphere electron transfer. Application of the Marcus theory to these reactions has permitted a calculation of the previously unknown redox potential for the compound II, native enzyme couple, and the homonuclear electron self-exchange rate between native enzyme and compound II. The values so obtained are 1.087 V and 7.5×10^{-5} M^{-1} s^{-1}, respectively, at pH 5.26 and 25 °C. The activation free-energy barrier for this self-exchange process is 23.2 ± 0.2 kcal mol^{-1}. The kinetics of the peroxidase-catalyzed oxidation of ferrocytochrome *c* can be accommodated by the Marcus theory as well if a more stable precursor complex is assumed for the cytochrome *c*–cytochrome *c* peroxidase reaction than for the reaction between the small inorganic complexes and the enzyme.

Cytochrome *c* peroxidase[1] is an enzyme present in yeast mitochondria which catalyzes the oxidation of ferrocytochrome *c* to ferricytochrome *c* by hydrogen peroxide according to the reaction sequence

$$\mathrm{CcP} + \mathrm{H_2O_2} \xrightarrow{k_1^{\mathrm{app}}} \mathrm{CcP\text{-}I}$$

$$\mathrm{CcP\text{-}I} + \mathrm{cyt}\ c'' \xrightarrow{k_2^{\mathrm{app}}} \mathrm{CcP\text{-}II} + \mathrm{cyt}\ c''' \tag{1}$$

$$\mathrm{CcP\text{-}II} + \mathrm{cyt}\ c'' \xrightarrow{k_3^{\mathrm{app}}} \mathrm{CcP} + \mathrm{cyt}\ c'''$$

Cytochrome *c* peroxidase, which has been the subject of a