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(29) Further work on the chemistry of **1** is in progress as well as X-ray analysis to prove that it contains a planar cyclooctatetraene.
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(31) H. C. Longuet-Higgins, "Aromaticity", *Chem. Soc., Spec. Publ.* **No. 21**, 109, 1967.
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(34) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962); **87**, 1345 (1965).
(35) If platinum oxide or palladium on charcoal from a fresh bottle was used, cleavage of the four-membered ring occurred. However, an old bottle of palladium on charcoal (Baker) was found which reduced only the double bond.

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# Stable Carbocations. CLXXVI.[1a] 3-Nortricyclyl Cations. Question of Charge Delocalization in Rigid Cyclopropylcarbinyl Systems[1b]

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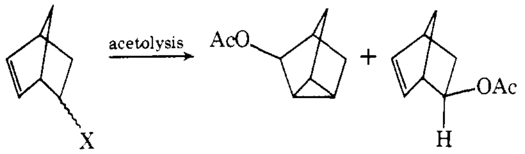
**Abstract:** A series of 3-nortricyclyl cations **1-R** (R = H, $CH_3$, $CH_2CH_3$, OH, $C_6H_5$, Cl and F) have been prepared under stable ion conditions and characterized by proton and carbon-13 NMR spectroscopy. NMR data indicate that both secondary and tertiary 3-nortricyclyl cations are classical carbenium ion with charge delocalization into the cyclopropyl ring. Steric factors and molecular rigidity of carbocations investigated are of great importance in dealing with the question of the mode of charge delocalization.

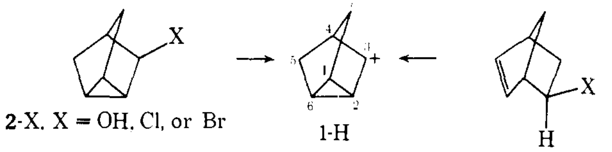
Solvolyses of esters of *exo*- and *endo*-2-norbornen-5-ols and 3-nortricyclanol have been of interest since the initial reports of their interconversion and reactivities by Roberts[2] and Winstein,[3] providing one of the key examples for homoallylic cations.[4] Strained $\delta$ bonds can provide very strong participation into transition states of solvolysis reactions.[5] Such interaction is particularly noticed in carbocations.[6] Among neighboring groups which are able to provide stabilization to adjacent carbocationic center, the effectiveness of the cyclopropyl group is well documented.[7] The interaction between strained cyclopropane $\delta$ bonds and the adjacent empty or developing p orbital is shown to reach its maximum in a bisected geometry,[6,8] which was confirmed by the direct observation of several long-lived cyclopropylcarbinyl cations.[9]



The cyclopropane ring in the geometrically rigid 3-nortricyclyl cations is situated in a favored bisected configuration toward the carbenium ion center for maximum charge delocalization. A preliminary carbon-13 NMR study[1b] however, showed that charge delocalization is more limited or not as effective as in the corresponding conformationally mobile cyclopropylcarbinyl cations.[9] Steric factors and rigidity in the studied system are therefore of great importance in dealing with the question of charge delocalization in carbocations. We have discussed extensively in our preceding work the question of $\delta$ bond delocalization in carbocations via two-electron, three-centered bond formation.[10] We also expressed our view that the mode of charge delocalization from trivalent carbenium ions to five-coordinated carbonium ions[11] is generally a continuous process with faster electronic movement being followed by slower nuclear reorganization. The extent of such deformation can vary greatly in different systems.

Although homoallylic participation[12] in the solvolysis of dehydronorbornyl-nortricyclyl type systems had received considerable attention in recent years,[13] the intermediate ions involved in the reactions have yet not been satisfactorily identified. The involvement of both unsymmetrical dehydronorbornyl (or norbornenyl) cations and symmetrical nortricyclyl cations had been discussed in an attempt to rationalize the overall product distribution in the solvolysis of these derivatives. In our preliminary studies, we have shown[1b] that the directly observed 3-nortricyclyl cations under stable ion conditions are symmetrically charge-delocalized, classical ions. We now wish to report in full our comprehensive investigation of the parent, as well as alkyl-, aryl-, and halogen-substituted 3-nortricyclyl cations.

## Results and Discussion



2-X. X = OH, Cl, or Br

1-H

3-X, X = OH or Cl

**Preparation of 3-Nortricyclyl Cations.** The parent, secondary 3-nortricyclyl cation **1-H** was generated from 3-nortricyclanol **2-OH**, or 3-chloro- or 3-bromonortricyclanes[13c,h] (**2-X**, X = Cl or Br) in $SbF_5$-$SO_2ClF$ solution at −78°. Attempts to prepare **1-H** cleanly from dehydronorbornane derivatives **3-X** (X = OH or Cl) were complicated by the complexation between the double bond and $SbF_5$ and consequently resulted in side reactions. Quenching solutions of ion **1-H** at −78° with potassium carbonate buffered ice-

Table I. Proton NMR Parameter of 3-Nortricyclyl Cations[a]

| Ion | $H_1,H_6$ | $H_2$ | $H_3$ | $H_4$ | $H_5,H_7$ | $\delta_{H_1} - \delta_{H_2}$ | Others |
|---|---|---|---|---|---|---|---|
| 1-H | 6.72 | 4.32 | 11.30[b] | 3.65 | 3.44[c] | 2.09 | |
| 1-$CH_3$ | 5.60<br>(d, 3.2) | 3.98 | | 3.50 | 3.28[c] | 1.62 | 3.48 ($CH_3$, s) |
| 1-$CH_2CH_3$ | 5.50<br>(d, 3.2) | 3.90 | | 3.40 | 3.21[c] | 1.60 | 3.75 ($CH_2$, q, 6.4)<br>1.68 ($CH_3$, t, 6.4) |
| 1-$C_6H_5$ | 4.61<br>(d, 3.4) | 3.85<br>(t, 3.4) | | 4.10 | 3.01[c] | 0.76 | 8.45 ($H_o$, d); 7.78 ($H_m$, dd); 8.32 ($H_p$, t)[d] |
| 1-OH | 3.85<br>(d, 4.6) | 2.50<br>(t, 4.6) | | 3.10 | 2.98[c] | 1.35 | 13.58 (OH, s); 13.98 (OH, s)[e] |
| 1-F[f] | 5.58<br>(d, 3.2) | 3.56<br>(t, 3.2) | | 3.34 | 3.59[c] | 2.02 | |
| 1-Cl | 5.94<br>(d, 3.8) | 4.42<br>(t, 3.8) | | 3.76 | 3.63[c] | 1.52 | |

[a] $^1H$ NMR shifts ($\delta$) are in parts per million from capillary $Me_4Si$. Multiplicities and coupling constants are given in parentheses; d = doublet, dd = doublet of doublets, s = singlet, t = triplet, q = quartet. [b] Doublet of doublets, $J_{2,3} = 4.4$, $J_{3,4} = 3.0$ Hz. [c] AB quartet. [d] $H_o$ = ortho, $H_m$ = meta, and $H_p$ = para protons. [e] The two OH resonances were observed at −78°. [f] $\phi_{^{19}F} = -148.5$ in parts per million from external $CCl_3F$.

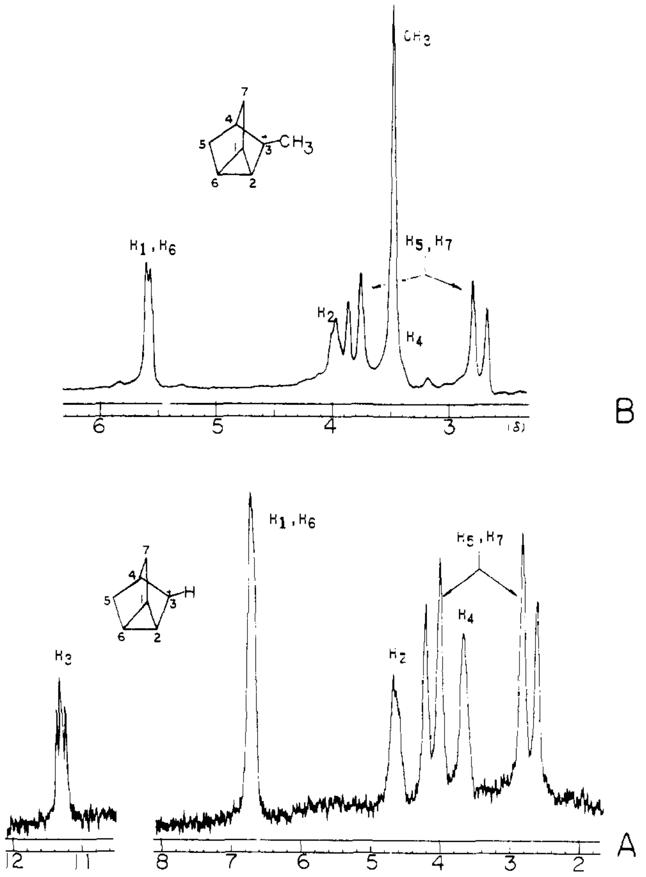


Figure 1. $^1H$ NMR spectra of the [(A) 60 MHz] 3-nortricyclyl and [(B) 100 MHz] 3-methyl-3-nortricyclyl cations in $SbF_5$-$SO_2ClF$ solution at −80°.

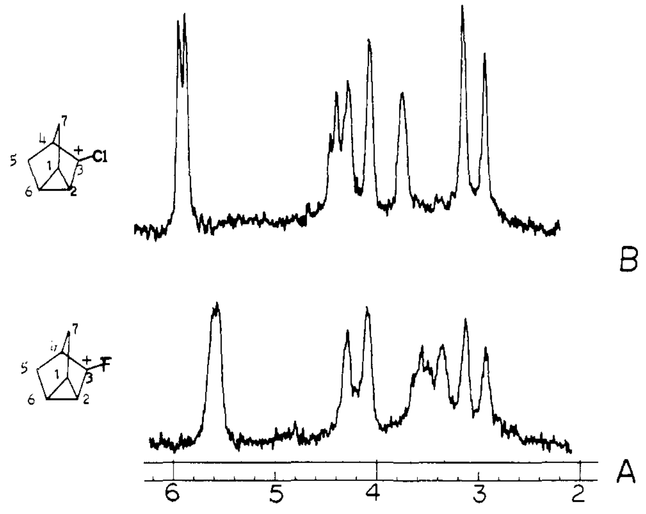
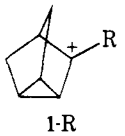


Figure 2. $^1H$ NMR spectra (60 MHz) of the (A) 3-fluoro- and (B) 3-chloro-3-nortricyclyl cations in $SbF_5$-$SO_2ClF$ solution at −80°.

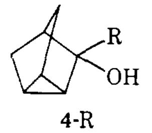
$SO_2ClF$ mixture gave 3-nortricyclanol and dehydronorbornanol (**2-OH** and **3-OH**, respectively) in a ratio of 4:1, along with some yet unidentified minor products.

The tertiary 3-nortricyclyl cations **1-R** (R = $CH_3$, $CH_2CH_3$, and $C_6H_5$) were prepared from their corresponding alcohols **4-R**[14] in either $FSO_3H$-$SbF_5$-$SO_2ClF$ or $SbF_5$-$SO_2ClF$ solution at −78°. All three ions **1-R** are stable below 0°, above which they slowly decomposed into unidentifiable decomposition products. Quenching of solutions of the ions with potassium carbonate-buffered ice-$SO_2ClF$ solution at −60° gave mainly the parent alcohols in about 45–50% yield. No olefinic products were detectable.

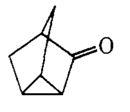


1-R

R = $CH_3$, $CH_2CH_3$, $C_6H_5$, and OH



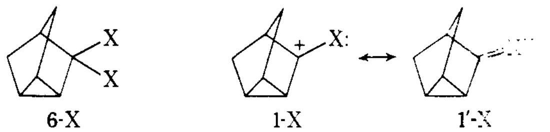
4-R



5

Protonated 3-nortricyclanone **1-OH** was obtained by the protonation of 3-nortricyclanone **5**[15] in either $FSO_3H$ or $FSO_3H$-$SbF_5$ solution diluted with $SO_2ClF$ at −78°. Quenching of solutions of **1-OH** with ice-water quantitatively gave back the starting ketone.

The 3-chloro- and 3-fluoro-3-nortricyclyl cations **1-X** (X = Cl and F, respectively) were prepared from the corresponding 3,3-dihalonortricyclanes **6-X** in $SbF_5$-$SO_2ClF$ solutions at −78°. 3-Chloro-3-nortricyclyl cation **1-Cl** is less stable than its fluorine analog **1-F**, which is sufficiently stable even at 20°.



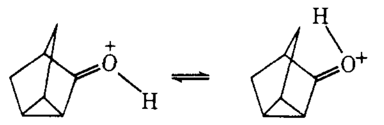
6-X 1-X 1'-X

X = Cl and F

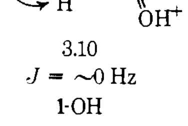
**$^1H$ NMR Study.** The $^1H$ NMR spectral parameters of the 3-nortricyclyl cations are summarized in Table I with their assignments. The $^1H$ NMR (50 MHz) spectra of **1-H**, **1-$CH_3$**, **1-Cl**, and **1-F** at −80° are shown in Figures 1 and 2, respectively. In general, the two equivalent cyclopropyl protons ($H_1$ and $H_6$) are about 1 to 2.5 ppm deshielded from the third one ($H_2$). The difference is greater in the case of secondary ion **1**-H than in the tertiary ions and apparently varies with the degree of charge delocalization into the cyclopropane ring. For the secondary ion **1**-H, $H_1$ and $H_6$ are deshielded by 2.1 ppm from that of $H_2$ while only by 1.5 ppm in case of tertiary ions (**1**-R), indicating more extensive charge delocalization in the former. The two sets of methylene protons in 3-nortricyclyl cations generally display an AB type quartet with coupling constants of the order of 12 Hz. The bridgehead protons ($H_4$'s) for both secondary and tertiary ions show absorptions at about $\delta$ 3.5 except that in **1**-$C_6H_5$, presumably because the bridgehead proton in the latter is in the deshielding region of the neighboring phenyl ring, as in the case of the 2-phenyl-2-norbornyl[10] and 2-phenyl-2-adamantyl[16] cations.

In the case of 3-halogen-substituted, tertiary cations **1**-Cl and **1**-F, the bridgehead proton $H_2$ and the two equivalent cyclopropane protons ($H_1$ and $H_6$) are more deshielded in the former than the corresponding protons in the latter ion. The other bridgehead proton $H_4$ in **1**-Cl is also found delocalized by 0.4 ppm from that in **1**-F. This observation is in agreement with our recent findings of the study of a series of halocarbenium ions.[17] Protons $\alpha$ to the carbenium ion center in chlorocarbenium ions are generally more deshielded than those in fluorocarbenium ions, indicating that more positive charge is shared by fluorine atoms via 2p-2p overlap than by chlorine atoms (**1**-X $\leftrightarrow$ **1'**-X). Furthermore, **1**-F shows a fluorine absorption at $\phi_{^{19}F}$ $-148.5$ in reasonable agreement with the fluorine absorption of cyclic and bicyclic fluorocarbenium ions, wherein fluorine "back-donation" to the carbenium centers prevails.[16,17]

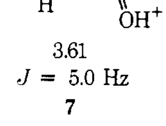
Protonation of tricyclic ketone *5*, according to its $^1H$ NMR spectrum (Table I), shows the presence of two isomers, indicated by the two downfield absorptions at $\delta$ 13.6 and 13.95. The two isomeric forms do not equilibrate until the solution is warmed to +20° and the two $=OH^+$ proton signals begin to merge into a broad singlet at $\delta$ 13.75. (The rest of the $^1H$ NMR spectrum shows only little change.) Several bicyclic ketones have been previously reported to form stable protonated species in superacid media.[18] In protonated bicyclo[2.2.1]heptanone **7**, a small coupling was observed between the bridgehead proton and the $H_{6,exo}$ ($J$ = 5.0 Hz). Protonated bicyclo[3.2.1]octanone-2[18] **8** does not show such coupling because of its slightly distorted geometry. In protonated bicyclo[2.2.2]octanone-2 **9**,[19] the bridgehead proton ($H_1$) only shows a broad resonance at $\delta$ 3.15. In the case of protonated 3-nortricyclanone, evidently no coupling exists between the bridgehead proton and $H_{5,exo}$. It is believed to be the consequence of the increased ring deformation caused by the incorporation of cyclopropane ring.



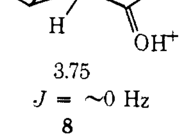
1-OH 1'-OH



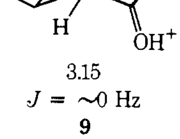
3.10
$J$ = ~0 Hz
1-OH



3.61
$J$ = 5.0 Hz
**7**



3.75
$J$ = ~0 Hz
**8**



3.15
$J$ = ~0 Hz
**9**

**$^{13}C$ NMR Study.** The complete noise-decoupled carbon-13 NMR spectra of the studied 3-nortricyclyl cations were obtained at −80° by the Fourier transform technique using a Varian XL-100 NMR spectrometer. Carbon shifts, multiplicities, and coupling constants ($J_{C-H}$ = Hz) are summarized in Table II along with assignments which were made with the aid either of their off-resonance or proton-coupled $^{13}C$ NMR spectra. The $^{13}C$ NMR spectrum obtained for the parent 3-nortricyclyl cation **1**-H is shown in Figure 3. There are, in general, five distinct carbon resonances for the nortricyclene framework for all 3-nortricyclyl cations, indicating that these ions are symmetrical. The carbenium carbon shifts are deshielded, with that of the secondary ion **1**-H found at the highest field (except the protonated ketone **1**-OH), those of 3-halo- and 3-phenyl-3-nortricyclyl cations at the intermediate, and 3-alkyl-3-nortricyclyl cations at the lowest field.

Although the cyclopropane ring carbons in the parent ion **1**-H are considerably deshielded from those in the tertiary cations, **1**-H is nevertheless a classical type of carbenium ion with a significant degree of charge delocalization into the cyclopropane ring. This is also indicated by the $>C^+$-H proton in the ion which is highly deshielded ($\delta$ 11.30).[20] The difference between the $C_1$ and $C_2$ shifts is larger in **1**-H (25.3 ppm) than in the tertiary ions (Table II, for example, 16.2 ppm for **1**-$CH_3$), indicating that more positive charge has been delocalized into the cyclopropane ring in the former. This is consistent with the $^1H$ NMR observation discussed above. For 3-halo-3-nortricyclyl cations, all of the carbon atoms of the nortricyclene framework of ion **1**-F are less deshielded than those in its chlorine analog (again in accordance with the $^1H$ NMR data). The strong 2p-2p interaction between fluorine and carbenium ion center therefore delocalized more positive charge unto the fluorine atom. There is also an unusually large coupling ($J_{C-F}$ = 420.2 Hz) observed between the carbenium carbon and the fluorine atom. Similar large $J_{C-F}$ values are also noticed in other acyclic and cyclic fluorocarbenium ions.[17]

**Structure of 3-Nortricyclyl Cations.** Winstein and his associates[7h,13d] have studied and discussed in detail the rates and product compositions of solvolyses of 2-dehydronorbornyl and 3-nortricyclyl derivatives. They have suggested that the symmetrically bridged cations cannot be the sole precursors for the formation of *exo*-dehydronorbornyl and nortricyclyl products. Slight differences in product composition may be due to solvolysis in the case of the dehydronorbornyl derivatives through an unsymmetrical cation and in the case of the nortricyclyl derivatives a symmetrical homoallylic cation. Winstein further suggested the following mechanism based on the fact that the nortricyclyl

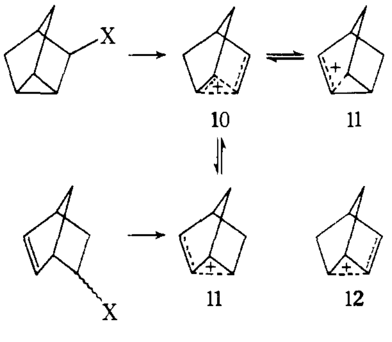


**Table II.** Carbon-13 NMR Parameters of 3-Nortricyclyl Cations[a]

| Ion | $C_1,C_6$ | $C_2$ | $C_3$ | $C_4$ | $C_5,C_7$ | $\delta_{C_1} - \delta_{C_2}$ | Others |
|---|---|---|---|---|---|---|---|
| 1-H | 111.6 | 86.3 | 258.5 | 42.4 | 46.6 | 25.3 | |
| | (d, 185.4) | (d, 204.9) | (d, 182.8) | (d, 175.2) | (t, 137.4) | | |
| $1\text{-}CH_3$ | 83.7 | 67.5 | 293.2 | 47.0 | 43.7 | 16.2 | 33.7 ($CH_3$, q, 133.2) |
| | (d, 198.0) | (d, 219.4) | (s) | (d, 170.5) | (t, 146.5) | | |
| $1\text{-}CH_2CH_3$ | 82.6 | 64.4 | 295.2 | 46.2 | 43.5 | 18.2 | 42.7 ($CH_2$, t, 129.0) |
| | (d, 181.3) | (d, 207.9) | (s) | (d, 163.0) | (t, 148.5) | | 10.0 ($CH_3$, q, 138.2) |
| $1\text{-}C_6H_5$[b] | 72.8 | 50.8 | 275.8 | 38.5 | 44.5 | 22.0 | 136.7 ($C_o$, d, 162.8); 135.8 ($C_o$, d. 166.4) |
| | (d, 190.2) | (d, 209.8) | (s) | (d, 168.0) | (t, 149.0) | | 132.0 ($C_m$, d, 167.5); 142.4 ($C_p$, d, 164.8) |
| | | | | | | | 130.5 ($C_i$, s) |
| 1-OH[c] | 38.2 | 41.3 | 223.8 | 44.1 | 28.0 | −3.1 | |
| | 38.1 | 41.4 | 221.5 | 43.1 | 27.1 | −3.3 | |
| 1-F | 74.1 | 47.7 | 258.0[d] | 40.2 | 42.0 | 26.4 | |
| | (d, 187.0) | (d, 208.4) | | (d, 169.1) | (t, 144.2) | | |
| 1-Cl | 84.1 | 69.0 | 267.8 | 49.4 | 43.6 | 15.1 | |
| | (d, 190.5) | (d, 204.8) | (s) | (d, 163.5) | (t, 145.2) | | |

[a] Carbon shifts ($\delta_{^{13}C}$) are in parts per million from external $Me_4Si$ (capillary). Coupling constants and multiplicities are given in parentheses, $J_{CH}$ in hertz; d = doublet, s = singlet, t = triplet, q = quartet. [b] $C_o$ = ortho, $C_m$ = meta, $C_p$ = para, and $C_i$ = ipso carbons. [c] Two isomers are observed at −78° which equilibrate at ca. 0°. [d] Carbenium carbon shift of 1-F shows a doublet centered at $\delta_{^{13}C}$ 258.0, $J_{CF}$ = 420.0 Hz.

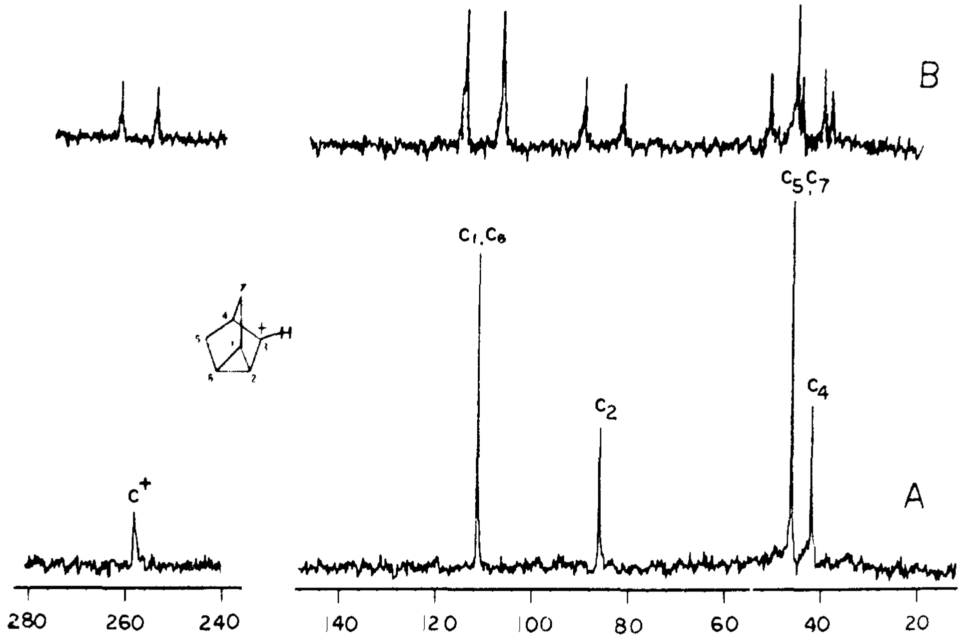


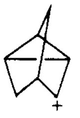
Figure 3. Carbon-13 NMR spectra of the 3-nortricyclyl cation: (A) proton noise decoupled; and (B) proton coupled.

derivatives undergo reaction to give *less* norbornenyl product than do the *exo*-norbornenyl derivatives so that the two different starting materials do not lead to the same intermediate cation. Consequent experiments lead to the conclusion that only the unsymmetrical cations are important in the solvolysis of both dehydronorbornyl and nortricyclyl derivatives.[13] In general, it is believed that in acetolysis (in acetic acid, a weakly acidic but strongly nucleophilic solvent), the equilibration of ions (**11** ⇌ **10** ⇌ **11**) is incomplete; whereas in formic acid (a more strongly acidic but weakly nucleophilic solvent), the equilibration process is expected to be essentially complete. Therefore the reaction intermediate for formolysis is expected to be more symmetrical than that for acetolysis. Furthermore, the structure **12** is preferred for the symmetrical dehydronorbornyl cation, suggested by Story.[12b]

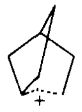
Recently, Arhart and Martin[21a] studied the reaction of isomeric mixtures of 3-nortricyclanol and *exo*-2-norbornen-5-ol with sulfurane derivatives in chloroform and found based on the lack of variation in product ratio that a common carbenium ion intermediate derived from the two isomers is involved. This seems to be not in accord with what is observed in solvolytic systems. Using the thiocyanate isomerization technique for trapping carbocationic intermediates, Spurlock and Cox[21b] have studied thermal interconversion between *exo*-5-norbornenyl and 3-nortricyclyl thiocyanates. They have found that the product mixtures obtained from the norbornenyl precursors tended to contain substantially greater amounts of the unrearranged *exo*-5-norbornenyl isothiocyanate than was ever detected from the nortricyclyl precursors. Consequently the dehydronorbornyl cations are considered to be best represented as delocalized ions. Recent studies by Cristol et al.,[22] however, remove the necessity for consideration of any unsymmetrical norbornenyl-nortricyclyl cation, as has been earlier proposed.

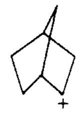
As interesting as solvolytic studies are, concerning their conclusion whether the intermediate dehydronorbornyl-nortricyclyl cations are of either symmetrical or unsymmetrical nature, this clearly depends on the degree of ionization, the acid strength, the nucleophilicity of the solvent systems, and possible ion-pair effect.[12] Under stable ion conditions, i.e., systems of high ionizing power and low nucleophilicity, the presently observed secondary and tertiary 3-nortricyclyl cations are apparently symmetrical with various degree of charge delocalization into the cyclopropyl ring.

The 3-nortricyclyl cation **1-H** was formally considered to be closely related to the parent secondary 2-norbornyl cation. The latter has been shown at low temperature to exist in its static, bridged carbonium ion (nonclassical) form.[10] No static, trivalent (classical) 2-norbornyl cation **13-H** has been observed to date. Should the 3-nortricyclyl cation **1-H** be considered as a nonclassical carbonium ion, similar to the 2-norbornyl cation? The $^1H$ NMR spectrum of **1-H** shows a highly deshielded proton resonance for $H_3$ at $\delta$ 11.30, which is in the characteristic region for protons directly attached to a carbenium ion (classical) center (i.e., $\delta$ 13.0 and 9.6 for dimethyl- and methylcyclopropylcarbenium ions, respectively). The stability of the secondary ion **1-H** is undoubtedly attributable to the significant delocalization of the positive charge into the cyclopropyl ring. The rigidity of the nortricyclyl framework however, prevents substantial bridging interaction[23,24] (see below). In contrast, the parent 2-norbornyl cation lacking such steric restriction is a truly nonclassical species involving intramolecular delocalization of the $C_1$–$C_6$ $\sigma$ bond with the formation a two electron, three-centered bond.[10] In addition, nonclassical carbonium carbons generally show highly shielded proton and carbon resonances, i.e., 2-norbornyl, 7-norbornenyl, and 7-norbornadienyl cations.[10] On the contrary, the 3-nortricyclyl cation **1-H** shows highly deshielded proton ($\delta_H$ 11.30) and carbon ($\delta_{^{13}C}$ 258.5) resonances for its carbocationic center, which are characteristic for a trivalent carbenium carbon with charge delocalization. It is, therefore, apparent that the 3-nortricyclyl cation does not possess nonclassical carbonium ion nature.



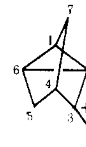
1-H



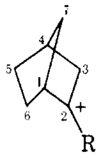


13-H

**Comparison of 3-Nortricyclyl and 2-Norbornyl Cations.** Since 3-nortricyclyl cations are closely related to 2-norbornyl cations, it is of interest to compare the NMR data of these two systems. Scheme I summarizes comparable $^{13}C$ NMR shifts of the two systems.

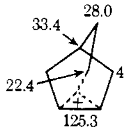


1-R

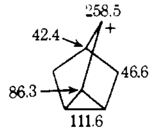


13-R

First of all, we shall compare the secondary 3-nortricyclyl and 2-norbornyl cations. For convenience, we have shown C NMR shifts by the structures. The difference between the classical ion **1-H** (with charge delocalization into the cyclopropyl ring) and the nonclassical ion **14** is clearly seen. The former, however, by no means should be considered a limiting nonclassical ion. It is simply a charge-delocalized *carbenium* ion.



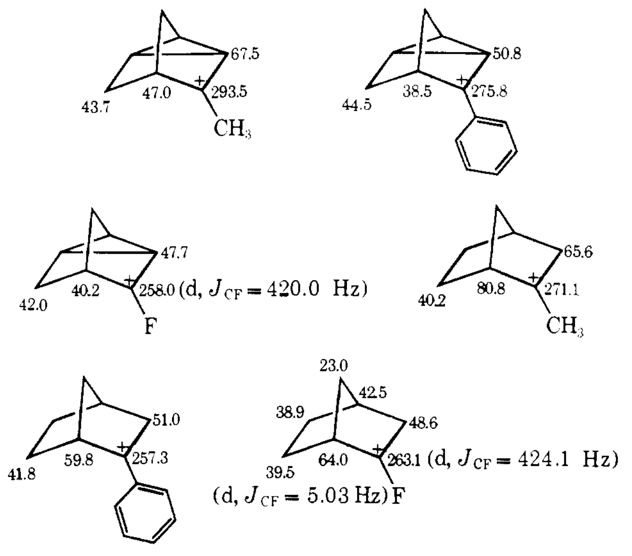
14



1-H

It always should be kept in the mind that whereas the differentiation of limiting trivalent (classical) carbenium ions from pentacoordinated (nonclassical) carbonium ions serves a useful purpose to establish the significant differences between these limiting ions, it is clear that in most specific systems there exists a continuum of charge delocalization.

Scheme I



Carbenium carbons ($C_2$) in tertiary 2-norbornyl cations are shielded from those in 3-nortricyclyl cations ($C_3$), except for fluorocarbenium ions, **1-F** and **13-F**. The bridgehead carbons ($C_1$) in the former are, however, much more deshielded from those ($C_4$) in the latter. For example, $C_2$ in **13-CH$_3$** is about 20 ppm shielded, and $C_1$ is about 30 ppm deshielded from the corresponding shifts ($C_3$ and $C_4$) in **1-CH$_3$**. The $C_6$ carbons in **13-R** are about 3 ppm less deshielded than the respective shifts ($C_5$ s) in **1-R**. The shielding of bridgehead carbons ($C_4$) in 3-nortricyclyl cations may result from two factors, namely: (1) more positive charge has been delocalized into the tricyclic structure in **1-R** than into the bicyclic structure in **13-R** so that $C_4$ in the former naturally experiences less inductive deshielding effect at carbon atoms directly attached to the electron deficient center; (2) $C_4$'s in **1-R** are located directly above the cyclopropane ring which should cause a shielding effect.[2] We have previously shown that the 2-methyl-2-norbornyl cation **13-CH$_3$** is a partially $\sigma$-delocalized classical carbenium ion.[10] The stronger conjugative effect from the cyclopropyl ring in **1-CH$_3$** might be more than sufficient to level off the $\sigma$ delocalization from the neighboring $\sigma$ bond ($C_4$–$C_5$) and consequently causes the bridgehead carbon to become shielded. The fact that **1-CH$_3$** shows a more deshielded carbenium carbon shift than that in **13-CH$_3$** might indicate that $C_1$–$C_6$ bond in the latter does delocalize positive charge via $\sigma$ delocalization, although increased ring strain might also shield the bridgehead carbon in the former.

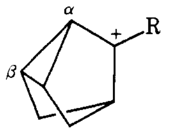
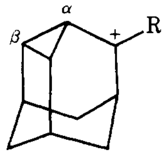
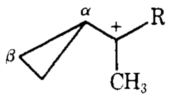
The phenyl group is known to be an effective neighboring group for stabilizing carbocations via p-$\pi$ conjugation. When the hydrogen is replaced by a phenyl group in **1-H**, the carbenium center should be further shielded since both cyclopropyl and phenyl rings would share the positive charge.[25] In contrast, the carbenium center in **1-C$_6$H$_5$** shows a carbon shift deshielded from that in **13-C$_6$H$_5$**. Models show that, in the 2-phenyl-2-norbornyl cation, the phenyl group would orient itself for favorable p-$\pi$ overlap with the empty p orbital so that one of the ortho protons would experience some nonbonded repulsion from the bridgehead proton ($H_1$); while both ortho protons of the phenyl group in 3-phenyl-3-nortricyclyl cation would suffer such steric repulsion with the bridgehead proton ($H_4$) and the cyclopropyl ring proton ($H_2$) would thus reduce the p-$\pi$ overlap between the phenyl ring and the empty p orbital which would consequently cause deshielding of the carbenium center (assuming that the phenyl-group substituent effect is the same in both systems).

Table III. Carbon-13 NMR Parameters of Cyclopropylcarbinyl Cations[a]

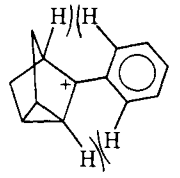
| Ion | $C_1,C_3$ | $C_2$ | $C_4$ | Others |
|---|---|---|---|---|
| **15**[b] | 57.1<br>(dd, 177.5, 180.0) | 108.3<br>(d, 180.0) | 57.1<br>(dd, 177.5, 180.0) | |
| 16 | 59.1<br>(dd, 175.5, 177.3) | 66.6<br>(d, 186.8) | 250.8<br>(d, 165.0) | 32.0 ($CH_3$, q, 129.7) |
| 17 | 53.5<br>(dd, 175.0, 177.5) | 56.8<br>(d, 185.0) | 281.9<br>(s) | 38.5 ($CH_3$, q, 132.5)<br>28.6 ($CH_3$, q, 127.5) |
| **18** | 50.7 | 60.3 | 281.6 | 41.2 ($CH_3$); 28.5 ($CH_2$); 12.2 ($CH_3$) |
| 19 | 45.1 | 45.9 | 246.3 | |
| **20** | 11.4 | 21.2 | 208.8 | 30.9 ($CH_3$) |

[a] Carbon shifts ($\delta_{^{13}C}$) are in parts per million from capillary $Me_4Si$. Coupling constants ($J_{CH}$ in hertz) and multiplicities are given in parentheses; d = doublet, dd = doublet of doublets, s = singlet, q = quartet, t = triplet. [b] Values for rapidly equilibrating carbenium ion.

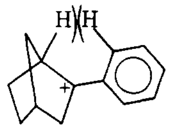
Table IV. Carbon-13 Shifts ($\delta_{^{13}C}$) for Cyclopropane and Carbenium Carbons in 3-Nortricyclyl, 8,9-Dehydro-2-adamantyl, and Cyclopropylcarbinyl Cations

| | |  | | |  | | |  | |
|---|---|---|---|---|---|---|---|---|---|
| R | $C_\alpha$ | $C_\beta$ | $C^+$ | $C_\alpha$ | $C_\beta$ | $C^+$ | $C_\alpha$ | $C_\beta$ | $C^+$ |
| H | 86.3 | 111.6 | 258.5 | 85.1[a] | 157.0 | 157.0 | 66.6 | 59.1 | 250.8 |
| $CH_3$ | 67.5 | 83.7 | 293.2 | 71.8 | 100.7 | 274.4 | 56.8 | 53.5 | 281.9 |
| OH | 41.3 | 38.2 | 223.8 | 42.0 | 67.8 | 240.9 | 21.2 | 11.4 | 208.8 |

[a] Rapidly equilibrating carbenium ion.



1-$C_6H_5$

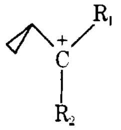


**13**-$C_6H_5$

The fluorine atom is also acknowledged as an effective neighboring group for charge delocalization and thus stabilizing fluorocarbenium ions[17] via p–p overlap between the fluorine 2p lone pair of electrons and the neighboring empty 2p orbital of the carbenium ion center. The fluorine atom is too small to produce any substantial nonbonded interaction with neighboring groups, as in the case of phenyl carbenium ions. Indeed, the carbenium center in **1-F** becomes slightly shielded from that in ion **13-F**.[26] Both fluorocarbenium ions show a $>C^+-F$ doublet with unusually large coupling constants ($J_{C-F}$) of the order of 420 Hz.

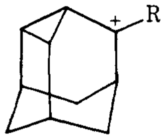
The comparison of the $^{13}C$ NMR data of 2-norbornyl and 3-nortricyclyl cations is thus instructive. When the substituents are varied from methyl to phenyl or fluorine in 2-norbornyl cations, a substantial shielding effect is found for the bridgehead $C_1$ carbons, while there is only a minimal variation for related bridgehead carbons $C_4$ in the 3-nortricyclyl cations. This indicates that the 2-methyl-2-norbornyl cation **13-CH**$_3$ indeed is stabilized by partial $C_1-C_6$ $\sigma$ delocalization as we have concluded previously.[10]

**Comparison of 3-Nortricyclyl, Cyclopropylcarbinyl, and 8,9-Dehydro-2-adamantyl Cations.** The 3-nortricyclyl cations are structurally related to their conformationally mobile analogs, the cyclopropylcarbinyl cations. We have previously reported the $^{13}C$ NMR spectra obtained by the INDOR method of these ions;[9,26] slightly modified and more accurate $^{13}C$ NMR parameters are now obtained by FT method. Table III gives the carbon-13 shifts, multiplicities, and coupling constants ($J_{CH}$ in hertz) of a series of cyclopropylcarbinyl cations **15–20** along with their assignments. The parent, cyclopropylcarbinyl cation **15** bears a fundamentally different structure from the methyl-substituted secondary and tertiary ions. The former has shown to be a rapidly equilibrating *nonclassical* ion; while the latter are *classical* carbenium ions with charge delocalization into the cyclopropyl ring.



**15**, $R_1 = R_2 = H$
**16**, $R_1 = CH_3$; $R_2 = H$
**17**, $R_1 = R_2 = CH_3$
**18**, $R_1 = CH_3$; $R_2 = CH_2CH_3$
**19**, $R_1 = CH_3$; $R_2 = C_6H_5$
**20**, $R_1 = CH_3$; $R_2 = OH$

Bisected geometry has been shown to be the most favored for the interaction between cyclopropyl ring and the neighboring carbenium ion center.[6] 3-Nortricyclyl cations have exactly this favorable conformation for maximum charge delocalization. Because of the rigidity of the tricyclic system, the more strained $\sigma$ bonds ($C_1-C_2$ and $C_2-C_6$) in 3-nortricyclyl cations should make bond delocalization between cyclopropyl ring and carbenium center more favorable than the less rigid system such as the cyclopropylcarbinyl cations. The carbenium ion centers ($C_3$) in 3-nortricyclyl cations, instead of experiencing more shielding effect, are deshielded from those in the corresponding cyclopropylcarbinyl cations. For 8,9-dehydro-2-adamantyl cations **21-R**,[1a] carbenium center ($\delta_{^{13}C}$ 274.4 for **21-CH**$_3$) is slightly upfield from that in cyclopropylcarbinyl cations ($\delta_{^{13}C}$ 281.9 for **17**). It is further noticed that carbons $\alpha$ to the carbenium center in the nortricyclyl and 8,9-dehydro-2-adamantyl



21-R
R = H, $CH_3$, and OH

cations are less deshielded than the $C_\beta$ carbons ($C_1$ and $C_8$ in **1-R** and **21-R**, respectively). The opposite trend is observed in the cyclopropylcarbinyl cations (Table IV). Steric inhibition of hyperconjugation is therefore important in concerning the matter of charge delocalization.

Recently, Hoffmann and Wilcox[7a] have indicated that cyclopropane is remarkably ineffective at transmitting resonance effects. However, the concentration of electron density at one site in its interacting HOMO by depleting the coefficients at other sites makes cyclopropane an excellent stabilizing group in the intensely conjugated cyclopropylcarbinyl systems. It is thus clear that hyperconjugative stabilization (electronic "vertical stabilization") must always be followed by nuclear movement and bond reorganization, the degree of which can, however, greatly vary and only in the limiting case lead to true bridging. In the rigid 3-nortricyclyl cations, bridging interaction between the strained C-C bonds of the cyclopropane ring and the empty p orbital ($\sigma$-$\pi$ interaction) is extremely limited. Thus it can be considered a more or less limiting example of charge delocalization with minimal nuclear movement. Based on experimental data, we thus agree with recent theoretical conclusions by Hoffmann et al.[27] on the strong conformational consequences of hyperconjugation, and that no dichotomy exists between charge delocalization in carbocations with or without significant nuclear reorganization ($\sigma$-bond delocalization or bridging vs. hyperconjugation or "vertical stabilization").[23]

Delocalization in carbocations can take place involving neighboring $\pi$ systems, $n$-donor substituents, of $\sigma$ bonds. There is in principle no difference between these systems. Development of an electron-deficient center in a carbocation inevitably will cause electron flow toward this center, and thus charge will delocalize over the molecule. Even in the $CH_3^+$ cation, there is charge delocalization into the C-H bonds, but of course its degree is much more limited than in other carbocations. It is thus rather meaningless to overemphasize the so called limiting "classical" or "nonclassical" nature of carbocations.

## Experimental Section

**Materials.** The 3-nortricyclanol, 3-nortricyclanone, 3-bromonortricyclane, 5-norbornen-2-ol, and 2-chloro-5-norbornene were prepared as previously described.[21,22,28]

3-Methyl-, 3-ethyl-, and 3-phenyl-3-nortricyclanols were prepared according to literature methods[13-15] from 3-nortricyclanone and corresponding Grignard reagent.

**Preparation of Ions.** A freshly prepared $FSO_3H$-$SbF_5$ (1:1) or a saturated solution of $SbF_5$ in $SO_2ClF$ was prepared and cooled to Dry-Ice-acetone bath temperature (ca. −78°). To the acid solution was then slowly added with vigorous stirring a cold solution of nortriclene precursors in $SO_2ClF$ to give an approximately 15-20% solution of the ion. The ionic solution was then immediately transferred into a precooled NMR tube.

**Proton and Carbon-13 NMR Spectroscopy.** $^1H$ NMR spectra were obtained using Varian Associates Model A56/60A and HA-100 NMR spectrometers, equipped with a variable-temperature probe. Tetramethylsilane was used as reference. $^{13}C$ NMR spectra were obtained using a Varian VFT, XL100-15 spectrometer equipped with a broad-band proton noise decoupler, and a variable-temperature probe. The instrument was operated in the pulse Fourier transform mode. Carbon shifts were measured from the $^{13}C$ signal of capillary $Me_4Si$ (5% enriched).

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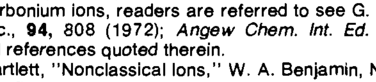
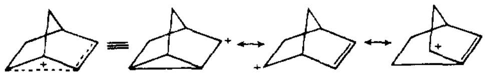
(20) One of the referees suggested that ion **1-H** might also exist as a rapidly equilibrating mixture of the nortricyclyl cation with the two related nor-



bornenyl cations. Such equilibration can, however, be excluded since it should give much more shielded carbon and proton shifts as an average of the involved systems. It is apparent that the 3-nortricyclyl cations are intensely charge delocalized as they can be expressed by the resonance forms



(not to be confused with a rapidly equilibrating formulation).

(21) (a) R. J. Arhart and J. C. Martin, *J. Am. Chem. Soc.*, **94,** 5003 (1972); (b) L. A. Spurlock and W. G. Cox, ibid., **93,** 146 (1971).

(22) (a) S. J. Cristol and D. A. Beimborn, *J. Am. Chem. Soc.*, **95**, 3651 (1973); (b) S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Jurale, ibid., **84**, 3918 (1962); (c) S. J. Cristol, T. C. Morrill, and R. A. Sanchez, ibid., **88**, 3087 (1966); *J. Org. Chem.*, **31**, 2719 (1966); (d) S. J. Cristol and R. W. Gleason, ibid., **34**, 1762 (1969).

(23) Traylor recently stated [D. F. Eaton and T. G. Traylor, *J. Am. Chem. Soc.*, **96**, 1226 (1974)] that his vertical delocalization concept was only meant as an extension of Winstein's original suggestion "that hyperconjugation and bridging were description of a single delocalization phenomenon involving little or much movement of the hyperconjugated or bridging group" [cf. S. Winstein, B. K. Morse, E. Grunwald, K. C. Schneiber, and J. Corse, ibid., **74**, 1113 (1952)]. The quoted paper does not seem to contain such a statement. The closest relevant part is note 19. "Participation amounts to delocalization of the $C_\beta$–R bonding electron pairs as electron deficiency is created by ionization. Now in hyperconjugation involving $\beta$ linkages, there is also delocalization. Whether, in general, hyperconjugation and participation should be considered to merge depends on the still unsettled preferred geometry in hyperconjugation."

(24) (a) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Am. Chem. Soc.*, **93**, 5715 (1971); (b) T. G. Traylor, R. S. Brown, and N. A. Clinton, ibid., **92**, 5228 (1970); (c) T. G. Traylor, H. J. Berwin, and W. Hanstein, ibid., **92**, 829 (1970); (d) T. G. Traylor and J. C. Ware, ibid., **89**, 2304 (1967).

(25) (a) G. A. Olah, P. W. Westerman, and J. Nishimura, *J. Am. Chem. Soc.*, **96**, 3548 (1974); (b) G. A. Olah and G. Liang, ibid., in press.

(26) G. A. Olah, P. R. Clifford, and C. L. Jeuell, *J. Am. Chem. Soc.*, **92**, 5531 (1970).

(27) R. Hoffmann, L. Radom, J. A. Pople, P. v. R. Schleyer, W. J. Hehre, and L. Salem, *J. Am. Chem. Soc.*, **94**, 6221, (1972).

(28) J. Meinwald, J. Crandall, and W. E. Hymans, *Org. Snyth.*, **45**, 74 (1965).

(28) (a) J. Meinwald, J. Crandall, and W. E. Hymans, *Org. Synth.*, **45**, 74 (1965). (b) E. Lippmaa, T. Pehk, and J. Paasivirta, *Org. Magn. Reson*, **5**, 277 (1973).

# Solvolysis of 3-Aryl-3-nortricyclyl *p*-Nitrobenzoates. Evidence for Major Increases in Electron Supply by the Cyclopropyl Group with Increasing Electron Demand at the Cationic Center[1]

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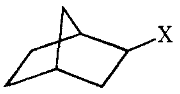
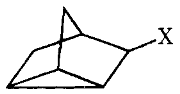
**Abstract:** Increasing the electron demand at the carbonium center by varying the substituent on the aryl group results in major increases in rates of solvolysis for the *p*-nitrobenzoates of 3-aryl-3-nortricyclyl, as compared with the corresponding 7-aryl-7-norbornyl derivatives. The rate increases must reflect major increases in the electron supply by the cyclopropyl moiety under the increasing demand of the cationic center. This conclusion is in contrast to previous interpretations that in the rigid 3-nortricyclyl cation interaction between the cyclopropane ring and the carbonium center is relatively limited. Comparison of the $\rho^+$ values for solvolysis of the *p*-nitrobenzoates of 7-aryl-7-norbornyl (−5.27) and 7-aryl-*anti*-norbornenyl (−2.30), isopropylmethylarylcarbinyl (−4.76) and cyclopropylmethylarylcarbinyl (−2.78), 2-aryl-*endo*-norbornyl (−3.75) and 2-aryl-*exo*-norbornyl (−3.83), 2-aryl-*endo*-norbornenyl (−4.17) and 2-aryl-*exo*-norbornenyl (−4.21), and 7-aryl-7-norbornyl (−5.27) and 3-aryl-3-nortricyclyl (−3.27) reveals a consistent pattern which lends confidence in this test for participation.

In investigations of the effect of structure on reactivity, the selection of a suitable model structure is crucial. The problem is clearly revealed by the 3-nortricyclyl system, which has been compared both with 2-norbornyl and 7-norbornyl, with opposite conclusions drawn.

For example, a comparison of the relative rates for **1** and **2** led to the conclusion that the ion from **2**, containing the cyclopropylcarbinyl moiety, does not exhibit stabilization, presumably because of steric difficulties inhibiting $\sigma$ bridging.[3]



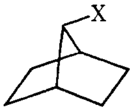
1



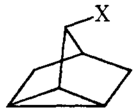
2

rel rate: 1.00 0.07

On the other hand, comparison of **3** and **4** reveals a major contribution of the cyclopropylcarbinyl moiety.[4] The fact is that **2** and **4** are identical. Yet opposite conclusions were reached as to the effectiveness of the cyclopropane ring in stabilizing the carbonium ion center through the particular selection of the model system.



3



4

rel rate: 1.0 $>10^8$

The effect of increasing electron demand at the carbonium ion center[5] offers the hope of reducing such ambiguities. This approach has previously been utilized to compare *exo*- and *endo*-norbornyl,[6] *exo*- and *endo*-norbornenyl,[7] and cyclopropylcarbinyl with the corresponding isopropyl moiety.[8] It appeared appropriate to apply this test to the 3-nortricyclyl system.

## Results and Discussion

A representative series of 3-aryl-3-nortricyclanols were synthesized by the reaction of the appropriate Grignard reagent with nortricyclanone. The products were converted to the *p*-nitrobenzoates, and the rates of solvolysis of the esters determined in 80:20 (v/v) acetone-water. The data are summarized in Table I.

The data follow the usual $\rho^+\sigma^+$ correlation[9] and yield a $\rho^+$ value of −3.27 (correlation coefficient 1.000). Irrespective of whether one utilizes 7-norbornyl or 2-norbornyl as the model, a comparison of the $\rho^+$ values clearly reveals resonance contributions from the cyclopropylcarbinyl moiety in the nortricyclyl system. An examination of the data now available lends confidence in this general approach.

The increase in $\rho^+$ from −5.27 for **5** to −2.30 for **6** reveals a large contribution resulting from $\pi$ participation.[5]