the isomer distribution that chlorine atoms are not involved—there is almost no reaction at the methyl group—nor is CCl_3 attack involved; there is neither $CHCl_3$ in the product nor an isomer distribution characteristic of CCl_3 attack.

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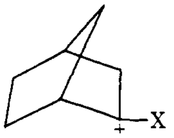
Received July 10, 1970

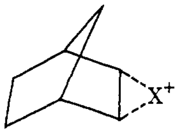
Stable Carbonium Ions. CXIII.[1] 2-Halonorbornyl Cations and Protonated 4-Halonortricyclenes

Sir:

2-Alkylnorbornyl cations have been demonstrated to be partially delocalized tertiary ions, whereas the unsubstituted norbornyl cation in superacids is symmetrically delocalized (corner-protonated nortricyclene).[2] In view of this difference in structure, we felt it would be of interest to study the 2-halonorbornyl cations (**1a–c**) which also could yield ions such as **2** and **3**.[3] We wish to report now our work in this regard and the observation of 2-halonorbornyl cations. In the course of this work we have observed a rearrangement which leads to 4-substituted nortricyclenes.



1a, X = F
b, X = Cl
c, X = Br



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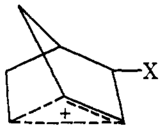

3

2,2-Difluoronorbornane (**4a**) when treated with SbF_5–SO_2 forms the 2-fluoronorbornyl cation (**1a**). The pmr spectrum of this cation is shown in Figure 1. The assignment of the pmr chemical shifts was made by comparison with those found for the 2-methylnorbornyl cation (**1d**) (Table I).[2] The cmr shift of C_2 in ion **1a** is −80.1 ppm (from CS_2), while the fluorine at C_2 has an ^{19}F resonance at ϕ −71.6 (from CCl_3F).

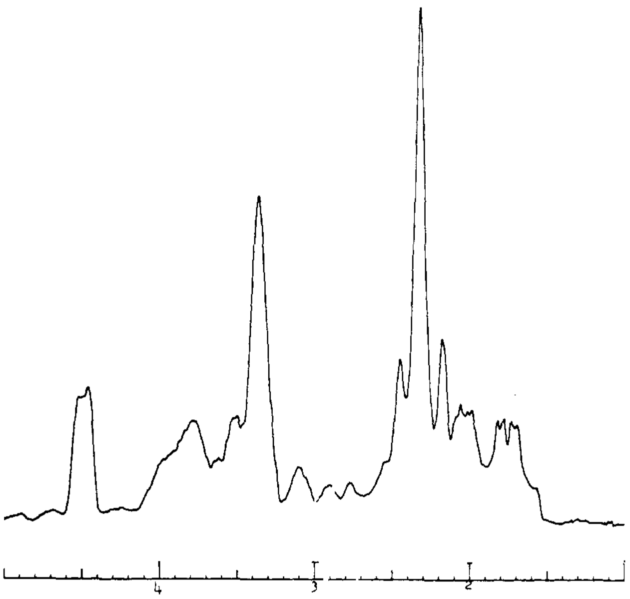

Figure 1. Pmr spectrum of 2-fluoronorbornyl cation in SO_2 at −70° (100 MHz).

Table I. Nmr Parameters of 2-Halo- and 2-Methylnorbornyl Cations in SbF_5–SO_2 Solution at −70°

	Pmr chemical shifts (δ)[a]								
Ion	CH_3	H_1	*exo*-H_6	*exo,endo*-H_3	H_4	H_7	*exo,endo*-H_5	*endo*-H_6	Cmr shift[b] C_2
1a		4.50	3.68	3.38 (br)	3.38 (br)	2.34	2.00	1.76	−80.1
1b		4.91	3.56 (br)	3.56 (br)	3.34	2.24	1.97	1.65	−92.1
1d	3.37	5.01	3.54	3.20	3.12	2.05	1.83	1.49	−76.1

[a] In ppm from capillary TMS. [b] In ppm from CS_2.

2,2-Dichloronorbornane (**4b**) in SbF_5–SO_2 solution at −78° gives a mixture of the 2-chloronorbornyl cation (**1b**) and protonated 4-chloronortricyclene (**5b**). Ion **5b** was identified by comparison of its proton (pmr) and ^{13}C (cmr) chemical shifts with those of protonated nortricyclene (Table II). Warming the solution to −25° produces no change in the distribution of the ions. Ion **1b** may be produced alone by treating **4b** with SbF_5 in SO_2ClF. Warming this solution to −15° does not produce any **5b**. Local heating during ion formation may be responsible for the formation of **5b** from **1b**. Ion **5b** is also obtained from 4-chloronortricyclene[4] (**6**) in FSO_3H–SbF_5–SO_2 solution at −78°.

When 3-bromonortricyclene (**7**) in SO_2 is added to FSO_3H–SO_2 and the resulting solution is treated with SbF_5, protonated 4-bromonortricyclene (**5c**) is obtained. The proton magnetic resonance spectrum at −70° is shown in Figure 2. As may be seen from Table II, both the pmr and the cmr chemical shifts compare favorably with those of protonated nortricyclene.[2]

On quenching ion **5c** with pyridine, 4-bromonortricyclene (**8**) is obtained. Ion **1c** is also obtained by treating 2,7-dibromonorbornane (**9**) and 2,3-dibromonorbornane (**10**) with SbF_5 in SO_2.

Both the 2-fluoronorbornyl cation (**1a**) and the 2-chloronorbornyl cation (**1b**) are stable partially delocalized norbornyl cations. Back-donation from fluorine and chlorine is sufficient to stabilize the 2-halonorbornyl cations. That the 2-fluoro substituent bears

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[1] Part CXII: G. A. Olah and G. Liang, *J. Amer. Chem. Soc.*, submitted for publication.

[2] (a) G. A. Olah and A. M. White, *ibid.*, **91**, 3954 (1969); (b) G. A. Olah, J. R. DeMember, C. Y. Lui, and A. M. White, *ibid.*, **91**, 3958 (1969); (c) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, **92**, 4627 (1970).

[3] Ions **2** and **3** have been postulated as intermediates in electrophilic additions to norbornene: T. F. Traylor, *Accounts Chem. Res.*, **2**, 152 (1969), and references therein.

[4] We wish to thank Dr. G. Dunn for a sample of 4-chloronortricyclene.

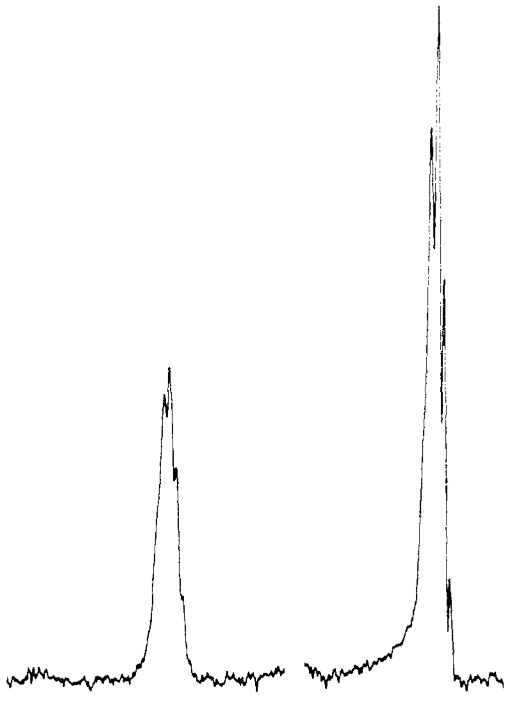
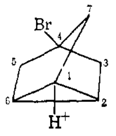
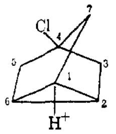
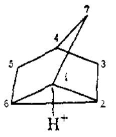


Figure 2. Pmr spectrum of protonated 4-bromonortricyclene in SO_2 at −70° (60 MHz).

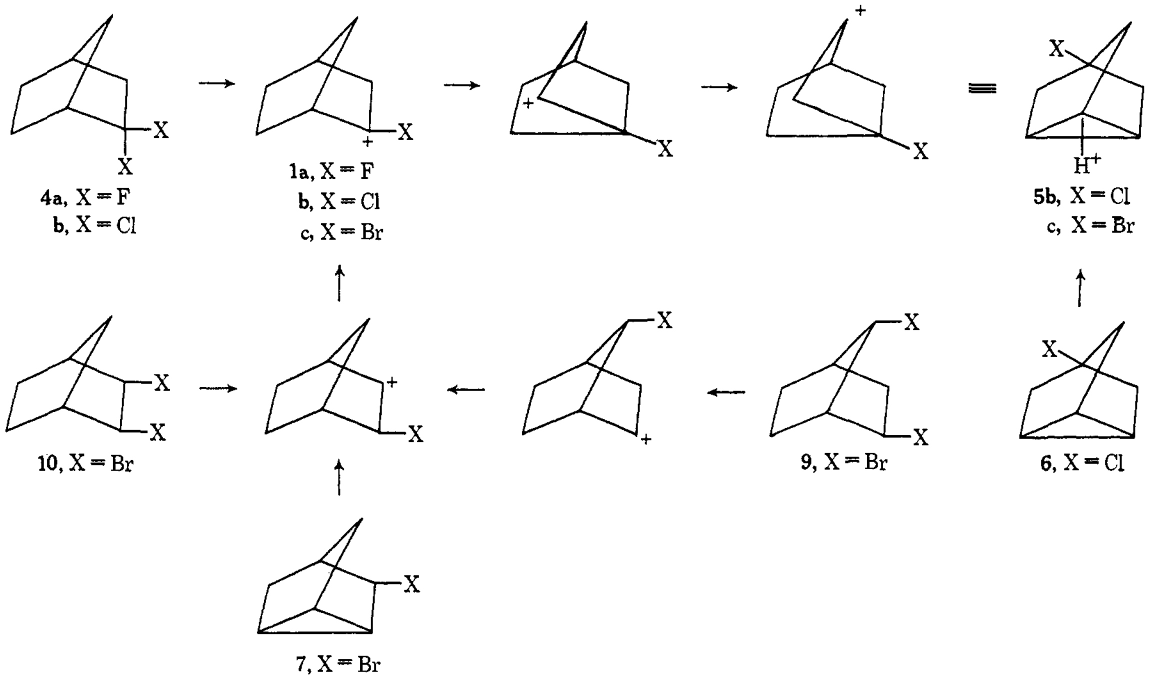
significant positive charge is demonstrated by the ^{19}F chemical shift of −71.6 (*cf.* ^{19}F chemical shifts of −181.91 and −51.48 ppm for $(CH_3)_2CF^+$ and $C_6H_5CF^+CH_3$, respectively[5]). The degree of delocalization in the 2-fluoro- and 2-methylnorbornyl (**1d**) cations is approximately the same. This is indicated by the cmr chemical shifts of C_2 in both ions when compared with the cmr chemical shifts of the sp^2 carbon of suitable models such as $(CH_3)_3C^+$ (−135 ppm from CS_2) and $(CH_3)_2CF^+$ (−142 ppm from CS_2). The $\Delta\delta_F{}^{13}C$ of −62.6 for the fluorine-substituted ions is quite close to that of $\Delta\delta_{CH_3}{}^{13}C$ = −58.9, where methyl is the substituent.[6] Furthermore, comparison of the cmr chemical shift of C_2 (−92.1 ppm) in the 2-chloronorbornyl cation (**1b**) with that of −120.0 ppm for the sp^2 carbon of $(CH_3)_2C^+{-}Cl$ ($\Delta\delta_{Cl}{}^{13}C$ = −27.9) indicates that ion **1b** is also a partially delocalized ion. Neither the 2-methylnorbornyl cation nor the 2-fluoronorbornyl

Table II. Nmr Parameters of Protonated 4-Halonortricyclenes in FSO_3H–SbF_5–SO_2 Solution at −70°

Ion	Pmr chemical shifts (δ)[a] H, H_1, H_2, H_6	H_3, H_5, H_7	H_4	^{13}C chemical shifts[b] C_1, C_2, C_6	C_3, C_5, C_7	C_4
	5.32	2.50		+101.7	+154.1	+144.3
	5.30	2.42		+100.4	+154.6	+132.0
	5.35	2.20	3.15	+101.8	+162.5	+156.1

[a] From capillary TMS. [b] In ppm from CS_2.

Scheme I



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[5] G. A. Olah and M. B. Comisarow, *J. Amer. Chem. Soc.*, **91**, 2955 (1969).

[6] $\Delta\delta_F = [\delta^{13}C^+(CH_3)_2{}^+CF - \delta^{13}C\ \mathbf{1a}] = [-142.7 - (-80.1)] = -62.6$. $\Delta\delta_{CH_3} = [\delta^{13}C^+(CH_3)_3C^+ - \delta^{13}C^+\ \mathbf{1d}] = [-135.0 - (-76.1)] = -58.9$.

cation rearranges to protonated 4-substituted nortricyclenes on warming.

The formation of protonated 4-substituted nortricyclenes from each of the precursors may be visualized as occurring by the pathways shown in Scheme I.

The Wagner–Meerwein shift of the C_1–C_6 bond to form bridgehead-substituted norbornanes has been used as the basis for the synthesis of 1-substituted norbornanes.[7] At present, 4-substituted nortricyclenes are prepared by multistep syntheses.[8] The ease of formation of 4-substituted nortricyclenes under stable ion conditions could lead to a synthetically useful method for the preparation of 4-substituted nortricyclenes *via* deprotonation by tertiary bases (a method proved successful in the case of protonated nortricyclene itself[2]).

Acknowledgment. Support of this work by a grant of the National Science Foundation is gratefully acknowledged.

(7) R. L. Bixler and C. Niemann, *J. Org. Chem.*, 23, 742 (1958).

(8) A partial description of the methods of synthesis of 4-substituted nortricyclenes may be found in J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *Tetrahedron*, 25, 369 (1969).

(9) (a) NIH Postdoctoral Research Fellow; (b) Postdoctoral Research Investigator.

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Received May 13, 1970

Observation of Coordinated Free Radicals Formed in the Reaction of Hydroxyl Radicals with Benzoatopentaamminecobalt(III) in Aqueous Solution

Sir:

The existence of radical transient species with finite lifetimes coordinated to the metal center has been proposed[1] to account for the kinetic behavior of pentaamminecobalt(III) complexes undergoing reaction with one-electron oxidizing agents such as Ce(IV). Despite efforts[2] to observe such species by esr, their transient nature and the presence of paramagnetic ions has apparently prevented their direct observation. We wish to report here the observation of a coordinated free radical transient formed in the reaction of OH radicals with $(NH_3)_5Co(O_2CPh)^{2+}$ using the pulse radiolysis technique.

A 30-nsec pulse of 2.3-MeV electrons[3] caused the radiolytic decomposition of water: $H_2O \rightsquigarrow 2.8e_{aq}^- + 2.8OH + 0.6H$. Saturation of the solution with N_2O (25 m*M*) resulted in the conversion of e_{aq}^- to OH: $e_{aq}^- + N_2O \rightarrow OH + N_2 + OH^-$. $Co(NH_3)_5(O_2CPh)(ClO_4)_2$ was prepared[4] from carbonatopentaamminecobalt(III) and benzoic acid in DMF according to a modification of the literature procedure.[5] Comparison of the absorption spectrum of the complex after recrystallization with that reported in the literature[6] indicated $<5\%$ impurities, presumably aquopentaamminecobalt(III) and free benzoic acid.

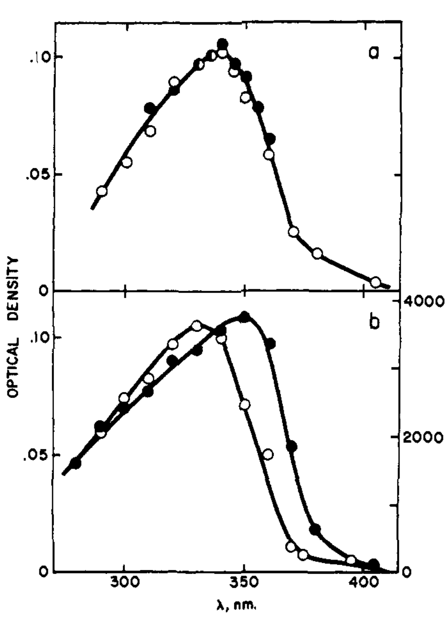

Figure 1. Absorption spectra from the pulse radiolysis of N_2O-saturated solutions: (a) 0.2 m*M* $(NH_3)_5Co(O_2CPh)^{2+}$ at pH 3.1, ●; pH 6.7, ○; dose/pulse, ~2.4 krads; (b) 1 m*M* NaO_2CPh at pH 3.1, ●; pH 9.0, ○; dose/pulse ~2.4 krads. These pH-dependent spectra are interconvertible at pH 4.4.

The transient absorption spectrum shown in Figure 1a results from the reaction of OH radicals with $(NH_3)_5Co(O_2CPh)^{2+}$. In comparison to this pH-independent spectrum (pH 3–7) with λ_{max} 340 nm, the spectra resulting from OH attack on free benzoate (λ_{max} 330 nm) and benzoic acid (λ_{max} 350 nm) are shown in Figure 1b. These latter two spectra have been assigned to the $\cdot C_6H_5(OH)COO^-$ and $\cdot C_6H_5(OH)COOH$ radicals,[7] respectively, with $pK_a = 4.4$ for the deprotonation of the carboxylate group.[8]

The reaction of OH radicals with the complex can result in three possible modes of attack: (1) addition of OH to the benzoato ligand; (2) dehydrogenation of an ammonia ligand; or (3) direct electron transfer from the metal center to form Co(IV). Comparison of the spectra from coordinated and free benzoate strongly indicates that process 1 predominates. The differences in the spectra indicate that reaction does not immediately cause labilization of the benzoato ligand in the form of its OH adduct. With regard to process 2, OH radicals apparently do not attack NH_4^+ in aqueous solution although NH_3 can be oxidized in alkaline medium;[9] the reaction of OH with free benzoate is very fast.[10] There is no reason to expect a drastic reversal of these rates due to complexation with Co(III). Furthermore, reaction of OH with $Co(NH_3)_6^{3+}$ generates a weak absorption tail in the 250–350-nm region.[11]

The complex radical transient decays *via* second-order kinetics with $2k = 9.3 \times 10^7\ M^{-1}\ sec^{-1}$ (pH independent) compared with $1.2 \times 10^9\ M^{-1}\ sec^{-1}$ for the OH adduct to benzoic acid and $4.4 \times 10^8\ M^{-1}\ sec^{-1}$

(1) R. Robson and H. Taube, *J. Amer. Chem. Soc.*, 89, 6487 (1967); J. E. French and H. Taube, *ibid.*, 91, 6951 (1969).

(2) H. Taube, *Advan. Chem. Ser.*, No. 49, 107 (1965), and discussion following; H. Taube, private communication.

(3) M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, 73, 3794 (1969).

(4) The authors thank Mr. E. R. Kantrowitz for the sample of the complex.

(5) E. S. Gould and H. Taube, *J. Amer. Chem. Soc.*, 86, 1318 (1964); E. S. Gould, *ibid.*, 87, 4730 (1965).

(6) W. E. Jones and J. T. R. Thomas, *J. Chem. Soc.*, 1482 (1966).

(7) R. Wander, P. Neta, and L. M. Dorfman, *J. Phys. Chem.*, 72, 2946 (1968).

(8) M. Simic and M. Z. Hoffman, manuscript in preparation.

(9) T. Rigg, G. Scholes, and J. Weiss, *J. Chem. Soc.*, 3034 (1952).

(10) M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotop.*, 18, 493 (1967).

(11) M. Z. Hoffman, unpublished observations.