

## Stable Carbonium Ions. X.<sup>1</sup> Direct Nuclear Magnetic Resonance Observation of the 2-Norbornyl Cation

Sir:

An unusually intensive research effort has been devoted to the study of bicyclo[2.2.1]heptyl cations, their rearrangements, rates of formation, and structure.<sup>2-11</sup> We wish to report the direct observation of the 2-norbornyl cation as the  $\text{SbF}_6^-$  salt in  $\text{SbF}_5$  or  $\text{SbF}_5$ -liquid  $\text{SO}_2$  solution,<sup>12</sup> the analysis of the n.m.r. spectra of such solutions,<sup>13</sup> and the discovery of new rearrangements in the norbornane series.

The n.m.r. spectra of 2-*exo*-norbornyl chloride and fluoride (I) are expectedly complex, but when either halide is dissolved in  $\text{SbF}_5$  or in  $\text{SbF}_5$ -liquid  $\text{SO}_2$  the same one-peak spectrum is observed at temperatures between  $-5$  and  $+37^\circ$  (Fig. 1). This broadened peak

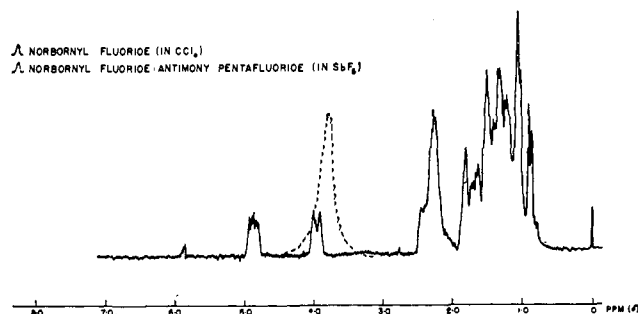


Fig. 1.—N.m.r. spectra of 2-*exo*-norbornyl fluoride (I, X = F) and the 2-norbornyl cation at  $+37^\circ$ .

appears near  $-3.75$  p.p.m. in neat  $\text{SbF}_5$  and near  $-3.1$  p.p.m. in  $\text{SbF}_5$ - $\text{SO}_2$ , relative to external tetramethylsilane. If the solution in  $\text{SbF}_5$ - $\text{SO}_2$  is cooled to  $-60^\circ$ , separation of the n.m.r. spectrum into three bands of areas 4 ( $-5.35$  p.p.m.), 1 ( $-3.15$  p.p.m.), and 6 ( $-2.20$  p.p.m.) occurs (Fig. 2). If the solution at  $-60^\circ$  is warmed to room temperature the single line pattern (at  $-3.1$  p.p.m.) is restored, and this warming-cooling cycle can be repeated many times, indicating the chemical stability of the ion in solution. The identity of this ion as the 2-norbornyl cation follows not only from the analysis of these n.m.r. spectra, discussed in the accompanying communication,<sup>13</sup> but

(1) Part IX: G. A. Olah, *J. Am. Chem. Soc.*, in press.

(2) S. Winstein and D. S. Trifan, *ibid.*, **74**, 1147, 1154 (1952); S. Winstein, *et al.*, *ibid.*, **74**, 1127 (1952); J. D. Roberts, C. C. Lee, and W. H. Saunders, Jr., *ibid.*, **76**, 4501 (1954).

(3) For work through early 1962, see J. A. Berson in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3, pp. 111-231.

(4) E. J. Corey and J. Casanova, Jr., *J. Am. Chem. Soc.*, **85**, 165 (1963); E. J. Corey, J. Casanova, Jr., P. A. Vatakencherry, and R. Winter, *ibid.*, **85**, 169 (1963).

(5) P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, Jr., *ibid.*, **85**, 479 (1963).

(6) H. C. Brown in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, pp. 154, 155, 175-178; H. C. Brown and F. J. Chloupek, *J. Am. Chem. Soc.*, **85**, 2322 (1963); H. C. Brown, F. J. Chloupek, and M.-H. Rei, *ibid.*, **86**, 1246, 1247, 1248 (1964).

(7) J. A. Berson and A. Remanick, *ibid.*, **86**, 1749 (1964).

(8) P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

(9) R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); *J. Am. Chem. Soc.*, **86**, 1259 (1964).

(10) C. A. Bunton, K. Khaleeluddin, and D. Whittaker, *Tetrahedron Letters*, 1825 (1963); P. Beltrame, C. A. Bunton, A. Dunlop, and D. Whittaker, *J. Chem. Soc.*, 658 (1964).

(11) W. Hüchel and M. Heinzl, *Tetrahedron Letters*, 2141 (1964).

(12) For experimental details, see G. A. Olah, E. B. Baker, J. C. Evans, W. S. Tolgyesi, J. S. McIntyre, and I. J. Bastien, *J. Am. Chem. Soc.*, **86**, 1360 (1964).

(13) M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964).

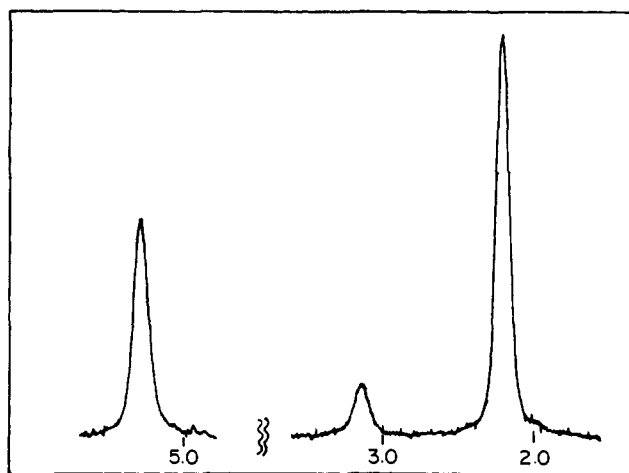


Fig. 2.—N.m.r. spectrum of the 2-norbornyl cation at  $-60^\circ$ .

also from the hydrolysis<sup>12</sup> of the ion, which produced only 2-*exo*-norbornanol (III) in good yield and in high purity.

The same 2-norbornyl cation can be generated in other ways and from other precursors. If 2-*exo*-norbornyl chloride (I, X = Cl) is dissolved in a solution of  $\text{AgSbF}_6$  in liquid  $\text{SO}_2$  containing a small amount of  $\text{SbF}_5$ , the same ionic species is formed. Treatment of norbornene (II) with  $\text{HSbF}_6$  ( $\text{HF} + \text{SbF}_5$ ) in  $\text{SbF}_5$  gives the same result. More surprising is the behavior of 1-chloronorbornane (IV) and 7-chloronorbornane (V), since both compounds are legendary in their inertness toward normal ionization conditions.<sup>3,8,14</sup> When either IV or V was dissolved in a solution of  $\text{SbF}_5$ - $\text{SO}_2$  at low temperatures, the n.m.r. spectra indicated little carbonium ion formation. When these solutions were warmed to  $-10^\circ$  and then cooled to  $-60^\circ$ , the characteristic 2-norbornyl signals (Fig. 2) were observed. The rearrangements of IV and V to the 2-norbornyl cation were confirmed by hydrolysis; both solutions gave principally 2-*exo*-norbornanol (III) (see Tables I and II). These rearrangements are without precedent in the literature.<sup>3,14</sup>

TABLE I

ANALYSIS OF HYDROLYSIS PRODUCTS FROM 7-CHLORONORBORNANE (V) IN  $\text{SbF}_5$ - $\text{SO}_2$

Hydrolysis after warming to ( $^\circ\text{C}$ .)	7-Norbornanol (VII), %	2- <i>exo</i> -Norbornanol (III), %
-50	70	30
-35	53	47
-20	5	95

TABLE II

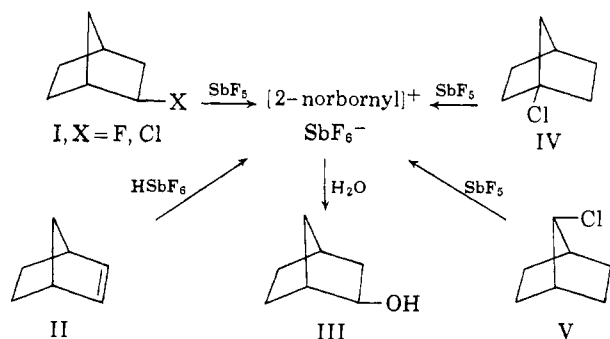
ANALYSIS OF HYDROLYSIS PRODUCTS FROM 1-CHLORONORBORNANE (IV) IN  $\text{SbF}_5$ - $\text{SO}_2$

Hydrolysis after warming to ( $^\circ\text{C}$ .)	1-Chloronorbornane (IV), %	1-Norbornanol (V), %	2- <i>exo</i> -Norbornanol (III), %	Other, %
-50	34	65	0.5	0.5
-35	1	11	87	1 <sup>a</sup>
-20	0	5	94	1 <sup>a</sup>

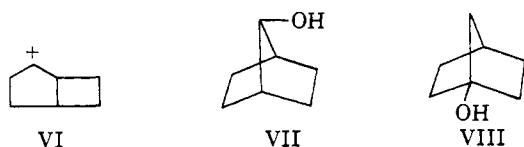
<sup>a</sup> Two minor products.

The fact that even simple aliphatic carbonium ions are stable in  $\text{SbF}_5$  solution suggests that such conditions should afford a maximum opportunity for rearrange-

(14) See P. von R. Schleyer and R. D. Nicholas, *ibid.*, **83**, 2700 (1961); R. C. Fort, Jr., and P. von R. Schleyer, *Chem. Rev.*, **64**, 277 (1964), and references therein cited.

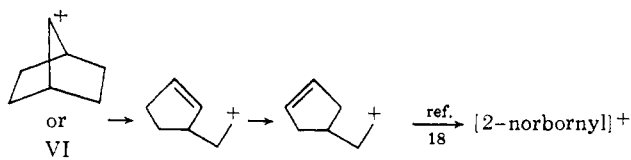


ment.<sup>12,15</sup> In a given series the carbonium ions of greatest over-all stability tend to form.<sup>12,15</sup> It is quite clear from the literature that the 2-norbornyl cation is considerably more stable than either the 1-norbornyl cation, the 7-norbornyl cation, or other bicycloheptyl cations of different carbon skeleton. One such structure is ion VI, which has been observed to be interconvertible with the 7-cation.<sup>16</sup> In an attempt to gain



some insight into the course of rearrangement of IV and V to the 2-norbornyl cation, we have carried out hydrolyses of solutions of these chlorides. The chlorides were dissolved in  $\text{SbF}_5\text{-SO}_2$  at  $-70^\circ$ , warmed to temperatures given in Tables I and II, cooled back to  $-70^\circ$ , and hydrolysed at this low temperature. Tables I and II summarize the data. From 7-chloro-norbornane (V) only 7-norbornanol (VII) and 2-*exo*-norbornanol (III) were obtained (Table I). 1-Chloro-norbornane (IV) was somewhat more inert.<sup>17</sup> At the lowest temperatures (Table II) some starting material was recovered. The major reaction products were 1-norbornanol (VIII) and III, although traces of unidentified substances were also detected by capillary gas chromatography.

We have no positive evidence for the mechanisms of the rearrangements of the 1- and 7-norbornyl compounds IV and V to the 2-norbornyl cation. The hydrolysis experiments suggest that the 1-norbornyl and 7-norbornyl cations are not interconvertible. The simplest conceptual mechanism for the transformation of IV to the 2-cation is a simple 1,2-hydride shift, while V might rearrange to the 2-cation either by a direct 1,3 hydride shift or by the fragmentation sequence shown below.



(15) Paul von R. Schleyer, R. C. Fort, Jr., W. E. Watts, M. B. Comisarow<sup>19</sup> and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 4195 (1964).

(16) S. Winstein, F. Gadiant, E. T. Stafford, and P. E. Klinedinst, Jr., *ibid.*, **80**, 5895 (1958).

(17) The acetolysis of 1-norbornyl tosylate is one-sixteenth the rate of 7-norbornyl tosylate: C. J. Norton, Ph.D. Thesis, Harvard University, 1955.

(18) R. G. Lawton, *J. Am. Chem. Soc.*, **83**, 2399 (1961); P. D. Bartlett and S. Bank, *ibid.*, **83**, 2591 (1961).

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(19) Alfred P. Sloan Research Fellow, 1962–1966; J. S. Guggenheim Fellow, 1964–1965; Fulbright Research Fellow, 1964–1965.

(20) National Science Foundation Predoctoral Fellow, 1963–1964.

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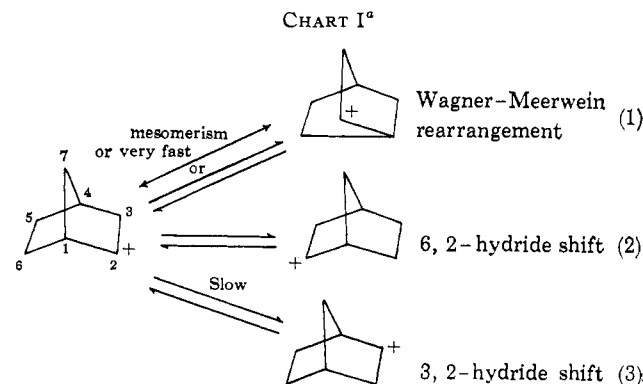
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## Stable Carbonium Ions. XI.<sup>1</sup> The Rate of Hydride Shifts in the 2-Norbornyl Cation

Sir:

The n.m.r. spectrum of the 2-norbornyl cation, as its  $\text{SbF}_6^-$  salt, undergoes significant changes with alteration in temperature. At  $-120^\circ$ , 2-*exo*-norbornyl fluoride in mixed  $\text{SbF}_5\text{-SO}_2\text{-SO}_2\text{F}_2$  solvent consists of three peaks at  $-321$  (area 4),  $189$  (area 1), and  $-132$  c.p.s. (area 6) from external tetramethylsilane (at 60 Mc.). No important change appears up to  $-60^\circ$ , but at higher temperature the peaks broaden and coalesce near  $-23^\circ$  to a single peak, which sharpens to 20 c.p.s. half-width at  $3^\circ$  (Fig. 1).<sup>1</sup> An analysis of these spectra allows us to determine the rates and activation parameters of hydride shifts occurring in the norbornyl cation.

Three rearrangements have been established for the 2-norbornyl cation.<sup>2</sup> These are the Wagner–Meerwein rearrangement (1), the 6,2- (or 6,1-) hydride shift (2), and the 3,2-hydride shift (3) (Chart I).



<sup>a</sup> For simplicity only classical carbonium ion formulas depict the rearrangements. This does not, however, *per se* imply any bias against the bridged (nonclassical) structure of the norbornyl cation.

The low-temperature spectrum is consistent with the assumption that (1) and (2) are proceeding rapidly and (3) slowly. The protons on carbons 1, 2, and 6 would interconvert rapidly, and they appear as the low-field peak of area 4 (A). The protons on carbons 3, 5, and 7 also would be equivalent, giving the high-field peak of area 6 (C). The single C<sub>4</sub> bridgehead proton gives the signal at intermediate field (B).

(1) Part X: P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5679 (1964).

(2) See ref. 2–11 of part X.<sup>1</sup>