$$I, X = F, Cl \xrightarrow{SbF_5} [2\text{-norbornyl}]^+ \xleftarrow{SbF_5} IV$$

ment.[12,15] In a given series the carbonium ions of greatest over-all stability tend to form.[12,15] 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.[16] In an attempt to gain

VI VII VIII
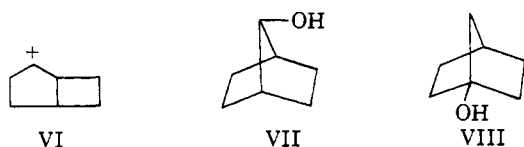
some insight into the course of rearrangement of IV and V to the 2-norbornyl cation, we have carried out hydrolyses of solutions of these chlorides. The chlorides were dissolved in SbF_5–SO_2 at $-70°$, warmed to temperatures given in Tables I and II, cooled back to $-70°$, and hydrolysed at this low temperature. Tables I and II summarize the data. From 7-chloronorbornane (V) only 7-norbornanol (VII) and 2-exo-norbornanol (III) were obtained (Table I). 1-Chloronorbornane (IV) was somewhat more inert.[17] 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.

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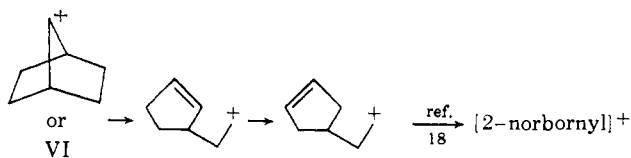
(15) Paul von R. Schleyer, R. C. Fort, Jr., W. E. Watts, M. B. Comisarow' and G. A. Olah, J. Am. Chem. Soc., **86**, 4195 (1964).

(16) S. Winstein, F. Gadient, 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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## Stable Carbonium Ions. XI.[1] The Rate of Hydride Shifts in the 2-Norbornyl Cation

Sir:

The n.m.r. spectrum of the 2-norbornyl cation, as its SbF_6^- salt, undergoes significant changes with alteration in temperature. At $-120°$, 2-exo-norbornyl fluoride in mixed SbF_5–SO_2–SO_2F_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 $-60°$, but at higher temperature the peaks broaden and coalesce near $-23°$ to a single peak, which sharpens to 20 c.p.s. half-width at 3° (Fig. 1).[1] 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.[2] 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).

CHART I[a]

mesomerism or very fast   Wagner–Meerwein rearrangement (1)

6, 2–hydride shift (2)

Slow

3, 2–hydride shift (3)
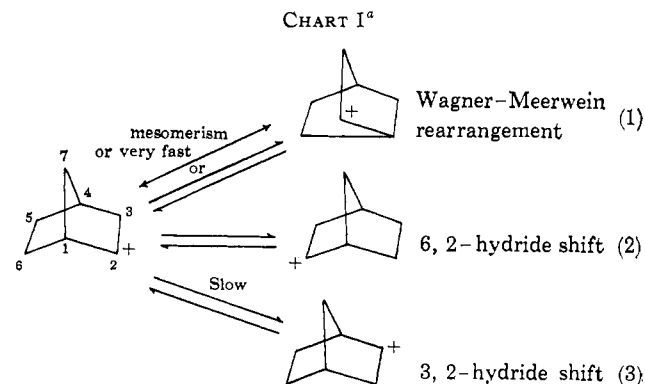
[a] For simplicity only classical carbonium ion formulas depict the rearrangements. This does not, however, per se imply, any bias against the bridged (nonclassical) structure of the norbornyl cation.
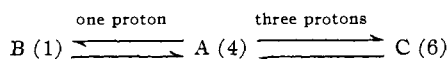
The low-temperature spectrum is consistent with the assumption that (1) and (2) are proceeding rapidly and (3) slowly. The protons on carbons 1, 2, and 6 would interconvert rapidly, and they appear as the low-field peak of area 4 (A). The protons on carbons 3, 5, and 7 also would be equivalent, giving the high-field peak of area 6 (C). The single C_4 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.[1]

At higher temperatures all rearrangements occur rapidly to render the hydrogens equivalent on the n.m.r. time scale. A single peak results.

Since the 3,2-hydride shift (3) is assumed responsible for interconversion resulting in a single line, it is this process which is most amenable to quantitative rate analysis. A single 3,2-shift transforms three of the A protons to C and one to B protons. The same 3,2-shift converts the B proton and three of the C protons to A protons. The line shape of the n.m.r. spectrum can be

$$B \ (1) \underset{\text{one proton}}{\overset{}{\rightleftharpoons}} A \ (4) \underset{\text{three protons}}{\overset{}{\rightleftharpoons}} C \ (6)$$

calculated readily when spin–spin coupling is not important.[3-6] Since the lines have less than 5 c.p.s. half-width at low temperature, this approximation should hold.[7] A general computer program coded in Fortran language has been written which allows the calculation using the number of sites, the relative transition probabilities, and the observed chemical shifts as input data.

Curves calculated for a series of rate constants agree well with spectra taken at different temperatures (Fig. 1). From these correspondences, the rates in Table I were obtained. The activation enthalpy for the 3,2-

TABLE I

CALCULATED RATES OF 3,2-HYDRIDE SHIFTS IN THE 2-NORBORNYL CATION

T, °C.	Half-width, c.p.s.	k, sec.$^{-1}$
+12.9	7.2	10,000
+ 7.0	12	6,000
+ 3.8	13.3	5,500
− 2.0	27	2,900
− 6.5	29	2,600
−11.2	51	1,550
−16.2	66	1,200
−19.3	98	850
−25.5	a	525
−29.0	a	375
−30.2	a	325
−33.5	a	225
−35.9	a	175
−38.2	a	150
−44.5	a	75
−46.0	a	72

a Rate determined from ratio of peaks when several peaks are present or from shape of collapsed spectrum.

hydride shift from the usual Arrhenius plot is $E_a = 10.8 \pm 0.6$ kcal./mole. The pre-exponential factor is $A = 10^{12.3}$ sec.$^{-1}$.

It is interesting to consider the information concerning the rates of processes 1 and 2. If these were slowed significantly at low temperatures, the low-field peak should have responded first by broadening. No such broadening was observed even at −120°. Assuming arbitrarily that the Wagner–Meerwein rearrangement (1) and the 6,2-hydride shift (2) occur at the same rate, the line shapes and half-widths of the low-field peak were calculated. A rate constant of 300,000 sec.$^{-1}$ or less should have produced an easily observable broadening of the low-field peak. We conclude that the rate of processes 1 and 2 must

(3) R. Kubo, Nuovo Chim., Suppl., 6, 1063 (1957).
(4) P. W. Anderson, J. Phys. Soc. Japan, 9, 316 (1954).
(5) R. A. Sack, Mol. Phys., 1, 163 (1958).
(6) M. Saunders, Tetrahedron Letters, No. 25, 1699 (1963).
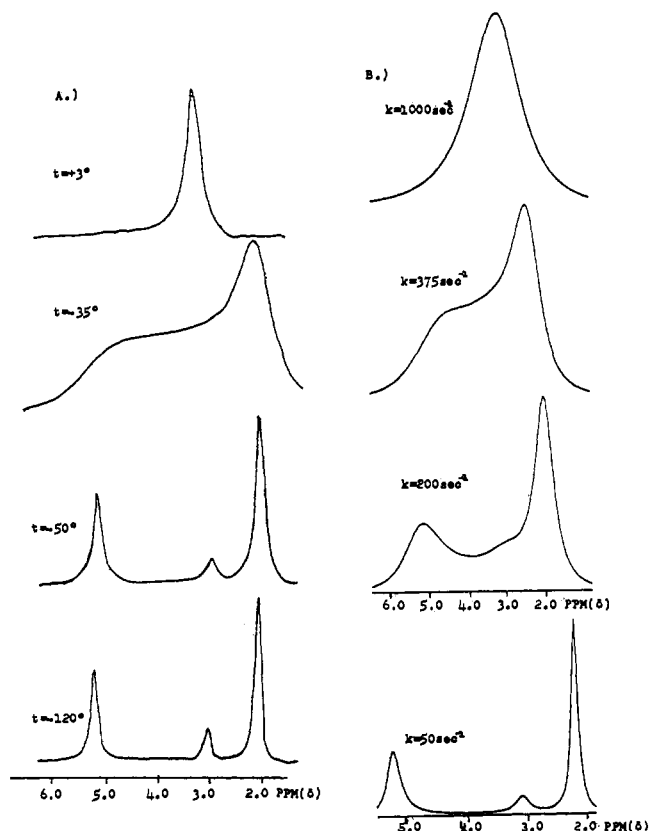(7) S. Alexander, J. Chem. Phys., 37, 967 (1962).

Fig. 1.—A. N.m.r. spectra of the 2-norbornyl cation at various temperatures. B. Calculated spectra for the 2-norbornyl cation for various rates of 3,2-hydride shifts.

be greater than this figure even at −120°. If the pre-exponential factor were 10^{13} for these processes, this would correspond to an activation energy less than 5.5 kcal./mole. Of course, with lower pre-exponential terms the limiting activation energy would be correspondingly higher.

At −120° the 3,2-hydride shift (3) is slower than the 6,2-hydride shift (2) and the Wagner–Meerwein rearrangement (1) by a minimum of $10^{8.8}$. In mixed SbF_5–SO_2ClF–SO_2 solvent we observed the spectrum of the 2-norbornyl cation at temperatures as low as −143°. Although there was a general line broadening of all peaks (probably due to the viscosity of the system), the extra line broadening of the low-field peak was still less than 5 c.p.s., corresponding to a minimum of the rate ratios in excess of 10^9. The large difference in the rates of these processes requires explanation in any consistent view of the nature of the norbornyl cation and the associated energy surface.[1,2]

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