

Rearrangement of Bicyclo[3.2.0]heptyl Precursors to the 7-Norbornyl Cation in the Cryogenic SbF_5 Matrix

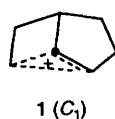
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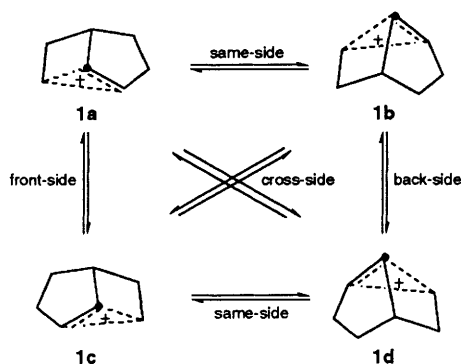
The first direct observation by IR spectroscopy in the cryogenic SbF_5 matrix was made of the rearrangement of 2- and 3-chlorobicyclo[3.2.0]heptanes (**3**) and (**4**), respectively, to the 7-norbornyl cation **1** and its subsequent transformation into the 2-norbornyl cation **5**.

The behaviour of 7-norbornyl derivatives is rather unique among secondary sulfonate esters. They are extremely unreactive even under forced solvolytic conditions,¹ the substitution products are >95% of retained configuration,² and the isolated rearranged products (<5%) are bicyclo[3.2.0]hept-2-yl derivatives³ in which—as shown by deuterium labelling studies—^{3,4} carbon atoms 2–3 and 4–5 interchange positions.

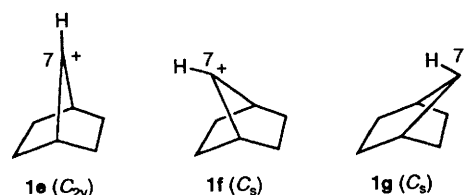
The exact structure of the intermediate carbocation was a long-standing problem in physical organic chemistry from the time of Winstein's proposal:^{1a,5} the observations can best be accounted for by the delocalized non-classical structure **1**.



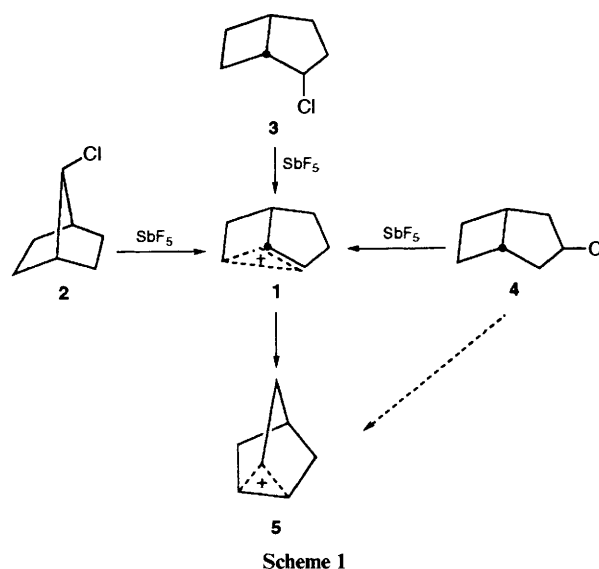
In a detailed study of this system Kirmse and Streu^{4a} proposed a dynamic equilibrium of four non-classical ions **1a–d**. This could explain partial racemization and deuterium relocation as well as the observed *anti*→*syn* leakage in the solvolysis of parent 7-norbornyl sulfonates.



A theoretical interpretation of the inherently low solvolytic reactivity based on orbital symmetry considerations was suggested in 1973 by Hoffmann, Mollere and Heilbronner.⁶ However, this argument strictly applies only to the symmetric C_{2v} structure for the solvolysis transition structure. Structure **1** could not offer a satisfactory explanation for the absence of a γ -isotope effect in 2,3-*endo*-deuteriated triflate, a structure closely related to 2-norbornyl derivatives where a normal kinetic deuterium isotope effect was observed in both 6-*exo* and 6-*endo* isomers.⁷ Early calculations on the semi-empirical and low *ab initio* level of theory showed structures of C_{2v} and C_s symmetry as possible energy minima.⁸ Attempts to isolate the 7-norbornyl cation under stable ion conditions in superacid media also failed.⁹ Both potential precursors, 7-norbornyl



chloride **2**, and bicyclo[3.2.0]hept-2-yl chloride **3** afforded the 2-norbornyl cation (**5**) as the only ion detectable by NMR (Scheme 1).



The enigma of the structure of this cation was eventually solved¹⁰ by a combination of high level *ab initio* calculation and low temperature matrix isolation technique which, as we have shown, can successfully be applied for the structural elucidation of elusive cationic reaction intermediates.¹¹ Calculations were performed at the MP4(sdq,fc)/6-31G*//MP2(full)/6-31G* + ZPE MP2(full)/6-31G* level. In the matrix isolation experiment a highly diluted mixture of 7-norbornyl chloride (**2**) and antimony pentafluoride (>1:500) was deposited on a CsI window at 10 K. By slowly warming the matrix to about 100 K, ionization to **1** occurred and the recorded IR spectrum was in very good agreement with the frequencies calculated for **1** at the correlated MP2(full)/6-31G* level. The calculated optimized structure is reproduced in Fig. 1.

According to theory, the C_s structure of the cation (**1f**) is a transition state which is 2.9 kcal mol⁻¹ higher in energy from the unsymmetrically bridged C_1 structure **1a–d**. Isotope and substituent rate effects can now be rationalized in terms of the

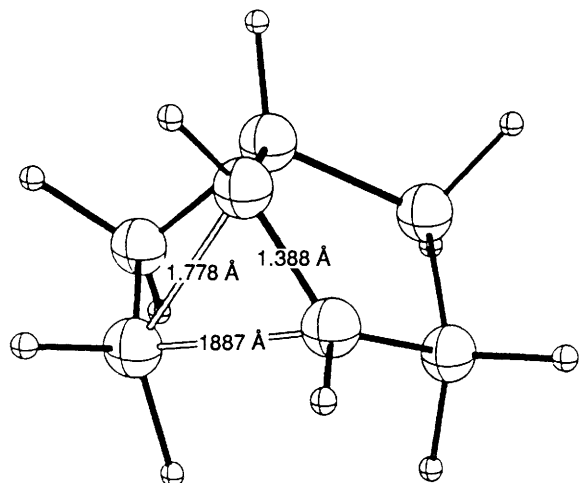


Fig. 1 7-norbornyl cation (1); MP2(full)/6-31G* optimized structure of C_1 symmetry¹⁰

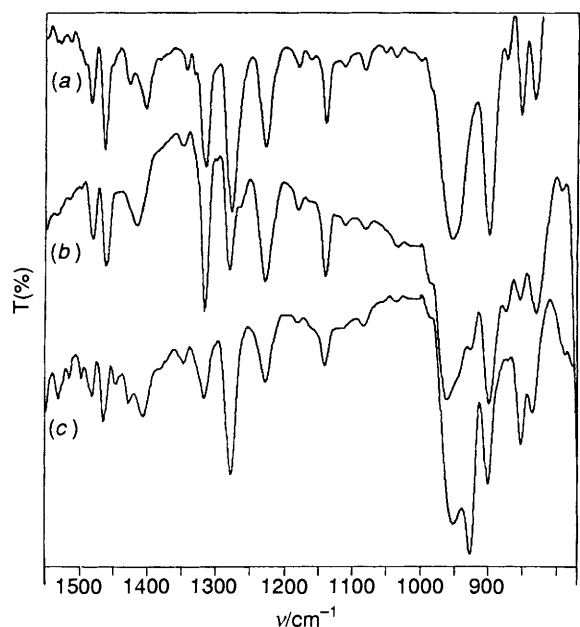


Fig. 2 Experimental and observed FTIR spectra of 7-norbornyl cation 1 generated from (a) 7-norbornyl chloride (2), (b) 2-chlorobicyclo[3.2.0]heptane (3) and (c) 3-chlorobicyclo[3.2.0]heptane (4) in the SbF_5 matrix

C_s structure where delocalization of charge to the underlying ribbon orbitals is still negligible.^{6,7}

The successful isolation of 1 in the matrix is due to the fact that this intermediate is separated from the global minimum on the $C_7H_{11}^+$ potential energy surface, the 2-norbornyl cation (5), by a barrier of 13.5 kcal mol⁻¹.¹⁰ However, in spite of an excellent correlation of theoretical and experimental frequencies ($m = 0.999$) some doubts still remain. The possibility, that the spectrum assigned to 1 *de facto* belongs to a complex of 2 with antimony pentafluoride was raised in a private exchange of correspondence with G. Olah and M. Saunders. The formation of 2- SbF_5 at very low temperatures could be preferred over the ionization to 7-norbornyl cation because of the relatively high activation energy required for the ionization of 2. However, from solvolysis studies^{3b,4} it is known that bicyclo[3.2.0]hept-2-yl derivatives are more reactive and also afford 7-norbornyl products presumably *via* the same cation 1. Thus, one may expect that the respective chloride (3) would be a better precursor for the preparation of 1 in the cryogenic matrix.

The present study was aimed to investigate this possibility

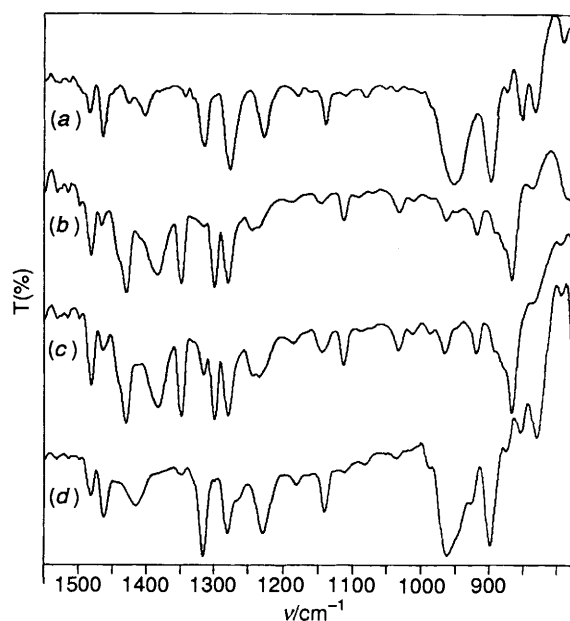


Fig. 3 FTIR spectra of 7- and 2-norbornyl cations respectively generated from 2 [spectra (a) and (b)] and from 3 [spectra (c) and (d)]

and also to find out if the isomeric bicyclo[3.2.0]hept-3-yl chloride affords the same ion under similar conditions.

Results and Discussion

When chlorides 3 or 4 were codeposited with SbF_5 under low dilution (5:1) on the CsI window cooled to 77 K, the recorded spectra corresponded to the starting materials. The spectral changes were observed after warming the matrix to 180 K. The spectra recorded at this temperature were assigned to 2-norbornyl cation 5, obtained in a separate experiment by ionization of 2-chloronorbornane.^{11b,12} However, by depositing 3 or 4 with a great excess of SbF_5 (500:1), the ionization to 7-norbornyl cation occurred already during the deposition. Both precursors afforded identical spectra as shown in Fig. 2. These spectra also agree with the spectrum from the previously published experiment with 7-chloronorbornane^{10a} and could unequivocally be assigned to the 7-norbornyl cation 1. Further rearrangement to 2-norbornyl cation occurs at 180 K. This is demonstrated by spectral changes shown in Fig. 3. All the observed rearrangements are summarized in Scheme 1.

While the ionization of 3 leads directly to cation 1, in the case of 4 the rearrangement to 1 is probably preceded by a hydride shift from C-2 to -3. Apparently this process has a very low barrier and proceeds *via* a hydrogen bridged cation which is, by analogy to the parent cyclopentyl cation,¹³ a highly reactive intermediate. At higher temperatures a direct rearrangement of 4 to 2-norbornyl cation 5 involving the participation of the C-1-C-7 bond is also feasible as shown by theoretical considerations.*

Experimental

In this work two procedures were used for deposition of the starting materials in the solid SbF_5 matrix *i.e.* under low (procedure A) and under high dilution (procedure B).

All IR spectra were recorded on a Perkin-Elmer 1725x FT-IR spectrometer with 2 cm⁻¹ resolution.

* Calculations by S. Sieber; we thank Professor P. v. R. Schleyer for this information.

Procedure A.—The flasks containing SbF_5 and the sample were loaded under nitrogen in a dry box then directly transferred to the depositing ports avoiding the use of any valves. The molar ratio of SbF_5 –substrate was approximately 5:1. The two small flasks were cooled by immersion in liquid nitrogen and the whole apparatus was evacuated by means of a mechanical pump to 0.001 Torr.* The deposition rate was regulated by changing the outer temperature of containers. In all experiments SbF_5 began to deposit during the first 2–3 min followed by the codeposition of both components. The maximal amount of SbF_5 used was 80–120 mg. At the end of the deposition, the apparatus was disconnected from the vacuum line and the shroud rotated 90° in order to achieve a proper alignment of the outer windows with the CsI window containing matrix. The warm-up procedure was initiated by removing liquid nitrogen from the cold finger. The spontaneous rise of the temperature was slow enough so that all changes in the spectrum of the sample could be observed by continuous recording.

Procedure B.—All the matrices were prepared in a closed cycle helium cryostat ROK 10-300 (Leybold Heraeus) connected to vacuum line equipped with the oil diffusion pump. During the deposition, the temperature was held at 10 K and vacuum at 10^{-5} – 10^{-6} Torr. The containers for SbF_5 and the sample were the same as in the procedure A. The flow of the sample was regulated by glass capillary (0.05 mm) and the flow of SbF_5 by immersion of the container in a cooling mixture (ice–water). The deposition times were 50 min in all the experiments. Matrix material (SbF_5) to sample ratio was estimated from the IR intensities of SbF_5 and sample signals.

7-Chlorobicyclo[2.2.1]heptane 2 and 2-Chlorobicyclo[3.2.0]heptane 3.—Compounds were prepared by published procedures.¹⁴

3-Chlorobicyclo[3.2.0]heptane 4.—Bicyclo[3.2.0]heptan-3-ol^{14c} (700 mg, 6.25 mol) was dissolved in dry diethyl ether (15 cm^3). To this solution were added 3–4 drops of pyridine and a solution of SOCl_2 (1.1 g, 9.37 mmol) in dry diethyl ether (5 cm^3). After being stirred under reflux overnight, the solvent and the rest of the SOCl_2 were evaporated. The remaining brown oil was dissolved in pentane and the solution was passed through a short Florisil column. After removal of the solvent, the pure product remained; yield 200 mg (24.5%); $\nu_{\text{max}}/\text{cm}^{-1}$ 2954, 2856,

1442, 1323, 1289, 1268, 1218, 915 and 793; $\delta_{\text{H}}(\text{CDCl}_3)$ 0.8–1.6 (8 H, m), 2–3 (2 H, m) and 4.5–4.7 (1 H, m).

Acknowledgements

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* 1 Torr \approx 133 Pa.