

Figure 2. Low-temperature ^{13}C CPMAS spectra of the 2-norbornyl cation. Spinning rates achieved range from 1.7 kHz at 120 K to 1.0 kHz at 6 K. In the 6 K spectrum, SS denotes a spinning sideband of the peak at 125 ppm.

predicted.¹⁴ As Saunders and Johnson have noted, the absence of side bands could be explained by very high frequency tunneling at all temperatures.^{11a} However, evidence that tunneling rates decrease with increasing temperatures^{12,13} makes this explanation less persuasive. One must also recognize that lattice effects which may destroy the symmetry of a hypothetical double-well potential further limit the possibility that tunneling is a valid interpretation. Alternatively, the spectra can be explained by an extremely low barrier or a single minimum potential surface. The absence of a significant barrier is exactly what the NMR data imply, and all that this kind of NMR experiment can establish.

The numerous studies of the 2-norbornyl cation have been reviewed and interpreted.¹⁵ Saunders's summation of experimental evidence supporting the bridged structure of the norbornyl cation^{11a} and the results of high-level ab initio calculations¹⁶ merit careful consideration. This study demonstrates CPMAS NMR capability at temperatures near that of liquid helium and provides further constraints on structural and dynamic hypotheses raised concerning the 2-norbornyl cation. We anticipate the use of ultralow-temperature MAS NMR in studies of other systems.

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(14) Spinning speeds were 1.7 kHz at 40 K and above. Spinning speed dropped slowly as the temperature was lowered and reached 1 kHz at 6 K. This change is reflected in spinning side bands which are identified in the spectra shown in Figure 2. Their presence should not interfere with identification of sidebands indicative of tunneling.

(15) For accounts of the classical vs nonclassical ion controversy, see: (a) Grob, C. A. *Acc. Chem. Res.* **1983**, *16*, 426. (b) Brown, H. C. *Acc. Chem. Res.* **1983**, *16*, 432. (c) Olah, G. A.; Surya Prakash, G. K.; Saunders, M. *Acc. Chem. Res.* **1983**, *16*, 440. (d) Walling, C. *Acc. Chem. Res.* **1983**, *16*, 448.

(16) (a) Ragavachari, K.; Haddon, R. C.; Schleyer, P. v. R.; Schaefer, H. F. *J. Am. Chem. Soc.* **1983**, *105*, 5915. (b) Yoshimine, M.; McLean, A. D.; Liu, B.; DeFrees, D. J.; Binkley, J. S. *J. Am. Chem. Soc.* **1983**, *105*, 6185. (c) Koch, W.; Liu, B.; DeFrees, D. J. *J. Am. Chem. Soc.* **1989**, *111*, 1527.

and grants from the Dreyfus Foundation and Research Corporation to Harvey Mudd College provided funding for the 200-MHz NMR apparatus used in synthesis and analysis of the labeled precursors.

Magic Angle Spinning Nuclear Magnetic Resonance Near Liquid-Helium Temperatures. Variable-Temperature CPMAS Studies of C_4H_7^+ to 5 K

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After four decades of detailed study, C_4H_7^+ remains enigmatic.¹ Recent high-level calculations show two isomers with nearly identical energy: the symmetrical bicyclobutonium ion (**1**) and a partially delocalized cyclopropylcarbanyl cation (**2**).² Further, these calculations indicate that the energy surface connecting **1** and **2** is quite flat.²

A set of interconversions, Figure 1, accounts for the rapid averaging of methylene carbons observed in solution-state NMR studies.³ If these interconversions could be slowed, **1** could be distinguished from **2** on the basis of chemical shifts of their unique methylene carbons. The pentacoordinate methylene of **1** should have a resonance at high field. The formally charged methylene of **2** should be strongly deshielded. We report here CPMAS spectral studies of C_4H_7^+ that provide the first direct spectral evidence for **1** and **2**.

Using the ultralow-temperature magic angle spinning NMR probe,⁴ we have obtained CPMAS spectra of methylene carbon labeled C_4H_7^+ in amorphous SbF_5 from 170 to 5 K. Spectra are shown in Figure 2. There is correspondence with earlier spectra above 77 K. Below 60 K, four distinct bands are seen at 235, 55, 28, and -15 ppm.⁷ The 235 ppm band intensity decreases and the upfield band at -15 ppm increases as the temperature is lowered to 5 K. The two bands at 55 and 28-23 ppm remain with little change. Short- and long-term temperature cycling showed that spectra are reproducible.

The development of distinct bands at 60 K and below requires slowing of a rapid equilibrium. IGLO (individual gauge for localized orbitals) calculations of the chemical shifts of **1** and **2** have been reported by Schindler,⁸ and calculated shifts, based on optimized geometries of **1** and **2** at the MP2(FULL)/6-31G* level,^{2b} are shown in Table I. Based on Schindler's calculated shifts and an array of supporting experimental data, we assign

(1) Brittain, W. J.; Squillacote, M. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1984**, *106*, 7280.

(2) (a) Koch, W.; Liu, B.; DeFrees, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 7325. (b) Saunders, M.; Laidig, K. E.; Wiberg, K. B.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7652. (c) McKee, M. L. *J. Chem. Phys.* **1986**, *90*, 4908.

(3) (a) Olah, G. A.; Kelly, D. P.; Juell, C. J.; Porter, R. D. *J. Am. Chem. Soc.* **1970**, *92*, 2544. (b) Olah, G. A.; Juell, C. J.; Kelly, D. P.; Porter, R. D. *J. Am. Chem. Soc.* **1972**, *94*, 7652. (c) Staral, J. S.; Yavari, I.; Roberts, J. D.; Surya Prakash, G. K.; Donovan, D. J.; Olah, G. A. *J. Am. Chem. Soc.* **1978**, *100*, 8018. (d) Staral, J. S.; Roberts, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 8020. (e) Saunders, M.; Siehl, H. U. *J. Am. Chem. Soc.* **1980**, *102*, 6868.

(4) (a) Hackman, A.; Seidel, H.; Kendrick, R. D.; Myhre, P. C.; Yannoni, C. S. *J. Magn. Reson.* **1988**, *79*, 148. (b) Myhre, P. C.; Webb, G. G.; Yannoni, C. S. *J. Am. Chem. Soc.*, preceding paper in this issue.

(5) Discussion of earlier spectral studies at 77 K and above will be included in our full report.

(6) A small peak near 235 ppm persists at higher temperatures. We believe this is due to an allylic ion isomer formed during annealing.

(7) At 60 K, additional bands at 104 ppm and a very sharp band at 40 ppm can also be resolved. The latter is assigned to a fraction of ions undergoing rapid exchange, and the former is assigned to ions undergoing more constrained exchange; see Table I and discussion in the text.

(8) Schindler, M. *J. Am. Chem. Soc.* **1987**, *109*, 1020.

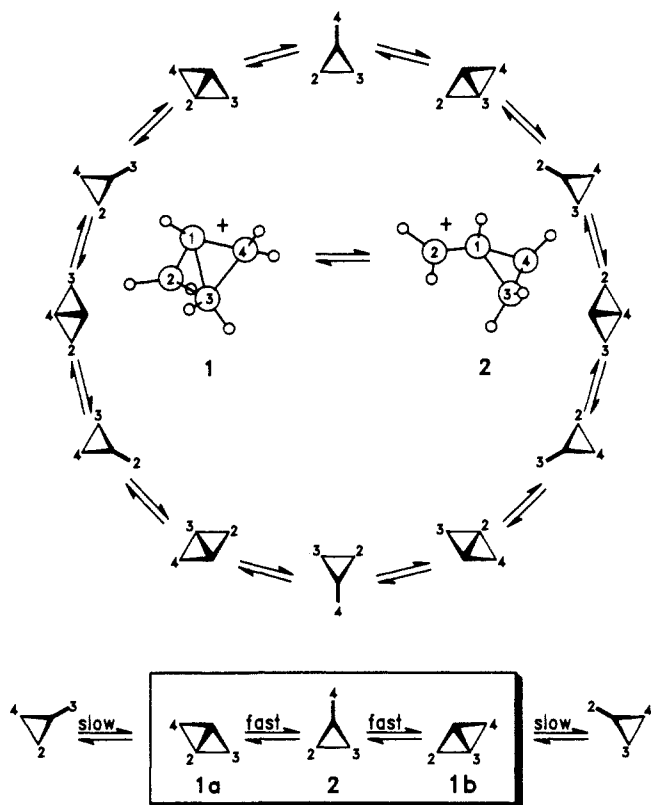


Figure 1. Projection drawings of interconverting bicyclobutonium ions (1) and cyclopropylcarbinyl cations (2). The projections show C1 above the plane of the paper. The projections were generated by holding the bond from C1 to the unique methylene of 1 fixed and allowing the unique methylene of 2 to swing to its position. The inset within the cycle shows representative three-dimensional drawings of 1 and 2 based on recent high-level calculations; see ref 2a. The inset at the bottom shows a representative constrained exchange (vide infra) where the unique methylene and one of the symmetrically related methylenes of 1 are averaged.

Table I. Comparison of Experimental^a and IGLO^b Chemical Shifts (ppm)

structure		CH ₂ ^c	CH ₂ ^d	(CH ₂) ^e	(CH ₂) ^f	(CH ₂) ^g
1	IGLO	67.1	-24.7	36.5	67	21
	expt, 60 K	55	-15	40	104 ^h	28 ^h
	expt, 15 K	55	-15	-	-	23
2	IGLO	65.8	245.2	125.7		
	expt, 60 K	-	235	-		

^a Estimated uncertainty ± 5 ppm. ^b Reported in ref 2b. ^c Symmetrically related methylenes. ^d Unique methylene. ^e Averaged methylenes under conditions of unconstrained rapid exchange; see text. ^f Unique methylene carbon shift under conditions of constrained exchange; see text. ^g Averaged methylene carbons under conditions of constrained exchange; see text and footnote 10. ^h See footnote 10.

the 235 ppm band to the unique methylene of 2 and the -15 ppm band to the unique methylene of 1.

The intensities of the 235 and -15 ppm bands allow estimates of K_{eq} for $1 \rightleftharpoons 2$ as a function of temperature.^{6,9} Conventional treatment indicates that ΔH° for this process is about +0.05 kcal mol⁻¹.⁹

The interconversion diagram provides a possible solution to the puzzling 28–23 ppm band. If 1 were constrained to a partial set of degenerate rearrangements, as shown in the inset of Figure 1, a different chemical shift averaging would obtain. Chemical shifts of 20 ppm for C2,C3 and 55 ppm for C4 are calculated for the equilibrating 1a and 1b with the use of experimental shift data (see Table I) and the assumption that the contribution of 2 can

(9) The assumption that simple equilibrium calculations apply to a glassy solid is a sweeping one; therefore, we take this estimate of ΔH° to be only qualitative.

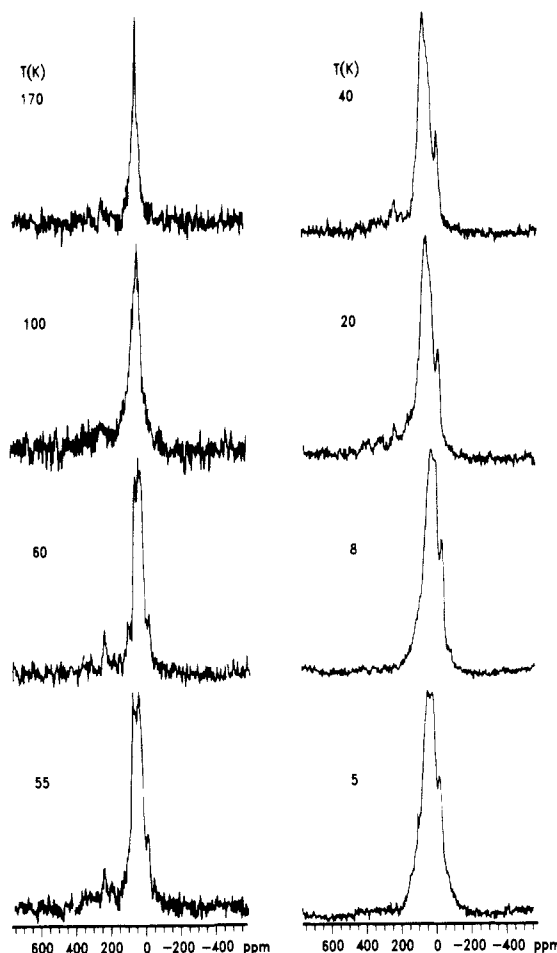


Figure 2. CPMAS ¹³C NMR spectra of C₄H₇⁺ in solid SbF₅ at various temperatures. Spinning rates achieved range from 1.9 kHz at 170 K to 800 Hz at 5 K.

be neglected. Inclusion of 2 (mole fraction 0.25) results in a marked downfield shift of C4 (to 100 ppm) and a small downfield shift of C2,C3 (to 29 ppm).¹⁰ With this explanation one can account for the spectra at all temperatures.

This explanation makes no sense in an isotropic medium, but it is credible in an anisotropic, glassy solid. It is not difficult to envision lattice sites or lattice-dictated orientations of a counterion that would facilitate exchange of 1a and 1b or inhibit exit from this subset of exchanges. Since the 23–28 ppm line assigned to C2,C3 of the constrained equilibrium persists at 5 K, the model proposed additionally requires that the energy surface connecting 1a, 2, and 1b be very flat, about a few tenths of a kilocalorie/mole. Presumably, the observation of static spectra result from a distribution of sites in the lattice and the attendant site-imposed barriers.¹¹

The notable result of this work is finding NMR spectral bands attributable to the bicyclobutonium ion and the cyclopropylcarbinyl

(10) The symmetrically related methylenes of 2 were assigned a chemical shift of 55 ppm.

(11) Broad distributions of carbocation degenerate rearrangement rates in solid SbF₅ allow visualization of some degenerate rearrangements with low barriers at quite high temperatures. The solution-state barrier for a hydride shift in the 2,3-dimethyl-2-butyl cation is about 3 kcal mol⁻¹. In solid SbF₅ the static spectrum of a fraction of the ions can be seen at 180 K (-93 °C)! See: Myhre, P. C.; Kruger, J. D.; Hammond, B. L.; Lok, S. M.; Yannoni, C. S.; Macho, V.; Limbach, H. H.; Vieth, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 6079.

(12) Professor J. D. Roberts has noted in a private communication that one could assign the three bands at -15, 23–28, and 55 ppm to the three different methylene carbons of an unsymmetrical bicyclobutonium ion. Apart from the apparent relative intensities of these bands over the 55–5 K range, there is no a priori reason to discount this interpretation, although adoption means that one must give little weight to recent theoretical results: see ref 2.

cation below 60 K. The estimated enthalpy difference between **1** and **2** in solid SbF_5 is very small. The barrier for interconversion of **1** and **2** cannot be determined, but it, too, must be very small to accommodate the observations.

The CPMAS NMR experiments and high-level *ab initio* calculations agree in major respects.² C_4H_7^+ is a mixture dominated by two structural isomers, the bicyclobutonium ion and the cyclopropylcarbinyl cation. Their energies are nearly identical, and the barrier to interconversion is very low. Characterized by experiment and theory, C_4H_7^+ is a molecular will-o'-the-wisp.

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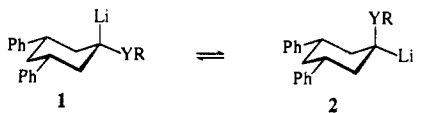
Lithium-Selenium Exchange. Stereochemistry of α -Lithio Selenides and Sulfides¹

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The preparation of organolithium reagents with stereochemical control at the C-Li center is generally successful only for a few structural types which are either configurationally very stable (vinyl,^{2a} α -alkoxyalkyl,^{2b} cyclopropyl^{2c}) or which show strong thermodynamic preferences for one stereoisomer because of chelation^{3,4,5a} or for stereoelectronic reasons (1,3-dithian-2-yl^{5b}). We report here the results of a stereochemical study of α -SeR and α -SR lithium reagents using the *cis*-3,5-diphenylcyclohexyl system **1**-**2**. Results that parallel some of ours have been obtained for several (γ -oxy- α -(phenylthio)propyl)lithium reagents^{3a,4a,b} and for (4-*tert*-butyl-1-(arylseleno)cyclohexyl)lithium.⁶



- a. YR = SePh
b. YR = SMe
c. YR = STol-*p*
d. YR = $\text{SeCH}_2\text{CMe}_2\text{CH}_2\text{SeBu-}t$
e. YR = H

Lithium reagents of this type are readily prepared by Li-Se exchange of selenoketals and selenothioketals.^{6,7} Compound **3a**

(1) (a) Reich, H. J.; Chow, F.; Shah, S. K. *J. Am. Chem. Soc.* **1979**, *101*, 6638. (b) Reich, H. J.; Green, D. P.; Phillips, N. H. *J. Am. Chem. Soc.* **1989**, *111*, 3444. Reich, H. J.; Phillips, N. H.; Reich, I. L. *J. Am. Chem. Soc.* **1985**, *107*, 4101.

(2) (a) Seyferth, D.; Vaughan, L. G. *J. Am. Chem. Soc.* **1964**, *86*, 883. Neumann, H.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2785. (b) Still, W. C.; Sreekumar, C. *J. Am. Chem. Soc.* **1980**, *102*, 1201. McGarvey, G. J.; Kimura, M. *J. Org. Chem.* **1985**, *50*, 4655. Cohen, T.; Bhupathy, M. *Acc. Chem. Res.* **1989**, *22*, 152. Rychnovsky, S. D.; Mickus, D. E. *Tetrahedron Lett.* **1989**, *30*, 3011. (c) Applequist, D. E.; Peterson, A. H. *J. Am. Chem. Soc.* **1961**, *83*, 862.

(3) (a) Hoffmann, R. W.; Bewersdorf, M. *Tetrahedron Lett.* **1990**, *31*, 67. (b) Hoffmann, R. W.; Bewersdorf, M.; Ditrich, K.; Krüger, M.; Stürmer, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1176.

(4) (a) McDougal, P. G.; Condon, B. D.; Laffosse, M. D., Jr.; Lauro, A. M.; Van Derveer, D. *Tetrahedron Lett.* **1988**, *29*, 2547. (b) McDougal, P. G.; Condon, B. D. *Tetrahedron Lett.* **1989**, *30*, 789. (c) Ritter, R. H.; Cohen, T. *J. Am. Chem. Soc.* **1986**, *108*, 3718.

(5) (a) Meyers, A. I.; Miller, D. B.; White, F. H. *J. Am. Chem. Soc.* **1988**, *110*, 4778. (b) Eliel, E. L.; Hartmann, A. A.; Abatjoglou, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 1807.

(6) (a) Krief, A.; Evrard, G.; Badaoui, E.; DeBeys, V.; Dieden, R. *Tetrahedron Lett.* **1989**, *30*, 5635. (b) Krief, A.; Dumont, W.; Clarebeau, M.; Bernard, G.; Badaoui, E. *Tetrahedron* **1989**, *45*, 2005.

(7) Seebach, D.; Meyer, N.; Beck, A. K. *Liebigs Ann. Chem.* **1977**, 846.

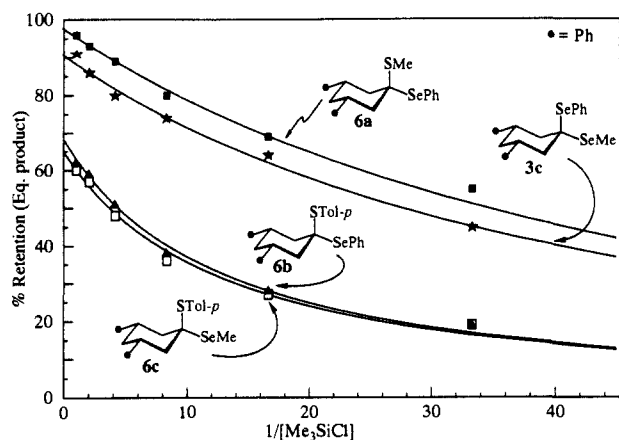
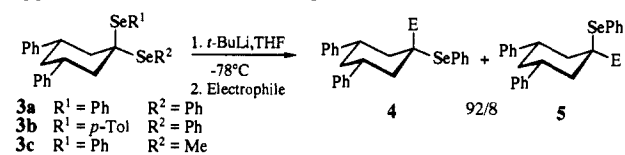


Figure 1. Product ratios for cleavage of selenides (0.01 M) by Li-Se exchange using *tert*-butyllithium in THF at -78°C with in situ trimethylchlorosilane. The lines represent simulations using two parameters: the ratio of second-order reaction of **2** with Me_3SiCl and first-order isomerization of **2** to **1** (k_2/k_1), and the initial stereospecificity (% equatorial formed initially): **6a** (■, $k_2/k_1 = 44$, 98%), **3c** (★, 39, 91%), **6b** (▲, 12, 69%), and **6c** (□, 13, 65%).

is cleaved rapidly by *n*-butyllithium to give lithium reagent **1a**, which can be quenched in excellent yield with a variety of electrophiles. The axial/equatorial product ratio was 92/8 within experimental error for the following electrophiles (% yield): EtCO_2H (E = H, 96), Me_2S_2 (93), *p*-Tol $_2\text{S}_2$ (72), *p*-Tol $_2\text{Se}_2$ (75), Me_3SiCl (91), $\text{Me}_2\text{iPrSiCl}$, CO_2 (77), CH_3CHO (81), pivaldehyde (78). Since these substrates differ greatly in reactivity and steric demands (note especially the pairs of silanes and aldehydes), we conclude that the 92/8 ratio represents the equilibrium mixture of axial/equatorial lithium reagents **1a/2a** and that these are being trapped faster than they can equilibrate.⁸



The stereoselectivity of the cleavage was also determined, using TolSe/PhSe compound **3b**.⁹ The products of cleavage and protonation were 93.3% **4-H**, 5% **5-H**, and 1.7% of the axially protonated *cis* H/TolSe compound. Thus the kinetic preference in favor of cleavage of the axial TolSe group ($\sim 98/2$)^{6a} is even larger than the thermodynamic ratio. The same conclusion can be reached from a different experiment. When **3a** was cleaved with *t*-BuLi in the presence of 48 equiv of trimethylchlorosilane, a 98/2 ratio of **4-SiMe₃/5-SiMe₃** was obtained (dimethyl sulfate gave similar results). We believe that under these conditions we are trapping the kinetic product ratio of **1a/2a**.

Support for the above interpretations was provided by studies of the PhSe/MeSe compound **3c**,⁹ using an in situ trimethylchlorosilane trap. The ratio of MeSe to PhSe cleavage was 4/1, so we were able to prepare the unstable equatorial lithium reagent **2a**.¹⁰ The interesting behavior summarized in Figure 1 was observed. A maximum of 91% of equatorial silane **5-SiMe₃** was formed when 96 equiv of trimethylchlorosilane was present, the fraction being a smooth function of $[\text{Me}_3\text{SiCl}]$. Thus the Li-Se exchange occurs with high retention of configuration, and trapping of **2a** and equilibration of **2a** to **1a** are competitive.

Lithium-selenium exchange is substantially faster than lithium-sulfur exchange.^{7,11} We can therefore study the fate of

(8) Trapping of nonequilibrium ratios of (α -(phenylthio)alkyl)lithium⁴ and (α -bromoalkyl)lithium reagents^{3b} with in situ carbonyl compounds or Me_3SiCl has been reported.

(9) This compound was prepared in isomerically pure form (>99%) by crystallization. This is an important advantage of the 3,5-diphenylcyclohexyl system over the traditional 4-*tert*-butylcyclohexyl locked cyclohexane.

(10) This effect was discovered by Krief^{6b} and has been used to prepare the less stable of two diastereomeric lithium reagents.^{3,6c}