

# Structure of the 7-Phenylnorbornyl Carbanion. A Pyramidal Organolithium and Planar Organopotassium

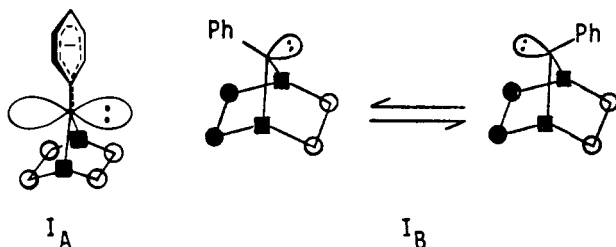
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**Abstract:** Solutions of (7-phenylnorbornyl)lithium, -potassium, and -cesium have been prepared in THF and the methods of sample preparation discussed. These benzylic ions are unstable at ordinary temperatures in ethereal solvent. The lithium derivative has been shown to be pyramidal by low-temperature carbon-13 NMR spectroscopy. The inversion process has been studied by NMR line broadening and the activation parameters determined:  $\Delta G^\ddagger_{205} = 9.4 \pm 0.2$  kcal/mol,  $\Delta H^\ddagger = 6.7 \pm 2$  kcal/mol, and  $\Delta S^\ddagger = -14 \pm 10$  gibbs. In direct contrast, the potassium and cesium salts give spectra which are consistent with a symmetrical planar benzylic carbanion. The rate determining step for inversion in the lithium derivative is attributed to ionic dissociation. These data are related to other literature work, and it is concluded that a simple carbanion is pyramidal, but with an inversion barrier of less than 5 kcal/mol.

A pyramidal carbanion is one of the fundamental structural concepts of organic chemistry<sup>1</sup> However direct experimental support for this concept is limited for carbanions in solution. The determination of the barrier to inversion has been restricted to cyclopropyl anions with strongly stabilizing substituents.<sup>2</sup> The present investigation was designed to provide more detailed information on carbanion inversion processes.

For solution studies, it is necessary to compromise between the influence of substituents on carbanion geometry and the need for stabilizing substituents to inhibit anion destruction by solvent deprotonation. Also, the question whether the substrate is sufficiently free of cation coordination to reflect the inversion process of the tricoordinate anion, or exists as the tetracoordinate organometallic, will depend on the choice of stabilizing substituent. The 7-phenylnorbornyl anion (I, 7-phenylbicyclo[2.2.1]heptyl carbanion) was selected for this study as a practical compromise. The symmetry difference between the planar ( $I_A$ ) and pyramidal ( $I_B$ ) structures of the anion should be readily detected by carbon-13 NMR spectroscopy. The NMR line-broadening phenomenon will also permit straightforward measurement of the rate of inversion in a pyramidal ion.<sup>3</sup>



## Experimental Section<sup>4</sup>

The following equipment and general procedures were employed. Materials were obtained from commercial sources. Melting points were

determined using a Thomas-Hoover or Fisher-Johns melting point apparatus and are uncorrected. Infrared (IR) spectra ( $\text{cm}^{-1}$ ) were recorded on a Perkin-Elmer 267 grating infrared spectrometer or a Beckman IR-33 grating infrared spectrometer and are referenced to either polystyrene ( $1601 \text{ cm}^{-1}$ ) or the spectrometer calibration ( $2000 \text{ cm}^{-1}$ ). Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra were recorded at 100 MHz (Varian XL-100). Carbon nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra were recorded at 20 MHz (Varian CFT-20), 25.2 MHz (Varian XL-100), or 37.7 MHz (Nicolet NT-150). Chemical shifts ( $\delta$ ) are reported in parts per million relative to tetramethylsilane ( $\text{Me}_4\text{Si}$ ) as an internal standard unless noted otherwise. Letters in parentheses refer to multiplicities in off-resonance decoupled spectra. Low- and high-resolution mass spectra were recorded on a Du Pont CEC-21-110B double-focusing mass spectrometer operating at a 70-eV ionization source. Gas chromatography work was performed on a Varian Aerograph 90P or F & M model 720 programmable chromatograph using helium as the carrier gas at ca. 60 mL/min.

Workup of reactions followed a routine procedure.<sup>4</sup> The reaction mixture was dissolved in equal volumes of ether and water. The aqueous layer was separated and extracted three times with ether (equal volumes). The combined ether layers were washed with acid (1 M HCl) and base (saturated sodium bicarbonate) where appropriate and then saturated sodium chloride ( $\sim 100 \text{ mL}$ ). The ether extract was dried over magnesium sulfate and evaporated with a water aspirator on a rotary evaporator using a water bath as heat source. Where special procedures were required, they are noted in individual preparations.

**7-Phenyl-7-methoxynorbornane.** The preparation of 7-norbornenone was adapted from the procedure of Gassman and Marshall<sup>5</sup> with a modified dechlorination step.<sup>6</sup> 1,2,3,4-Tetrachloro-7,7-dimethoxynorbornene<sup>5</sup> was dried and purified by fractional distillation prior to use. Ketal purity has a significant effect on yield. In a 3-L three-necked round-bottomed flask equipped with a mechanical stirrer and a pressure equalizing addition funnel (vacuum flame dried) was prepared a solution of sodium metal (39.4 g, 1.71 mol) in liquid ammonia (ca. 2.5 L) under nitrogen. To this ammonia/metal reducing medium, maintained in a  $-78^\circ\text{C}$  bath, was added a homogeneous solution of the tetrachloro ketal (49.5 g, 0.169 mol), anhydrous ether (375 mL) and absolute ethanol (41 mL, 4.1–4.5 equiv) at a moderate rate.<sup>7</sup> When the addition of this solution was complete, an additional 4 equiv of absolute ethanol was added and the reaction then allowed to stir for 30 min. Excess sodium was quenched by the slow addition of solid ammonium chloride ( $\sim 120 \text{ g}$ ), until the blue color was discharged, followed by an additional 5 g to destroy any sodium amide which may have formed. The ammonia was allowed to evaporate overnight. Routine workup followed by vacuum distillation ( $70\text{--}78^\circ\text{C}$  (22 mm), lit.<sup>5</sup>  $58\text{--}68^\circ\text{C}$  (17 mm)) gave 7,7-dimethoxynorbornene (12.9 g, 62% yield) as a colorless oil.

Conversion of the ketal to 7-norbornenone and addition of phenyllithium at  $-78^\circ\text{C}$  in THF to form 7-phenyl-7-norbornenol followed literature procedures.<sup>5,8</sup> A 3.2:1 mixture of syn and anti alcohols,<sup>9</sup>

(1) For reviews see: (a) Cram, D. J. "Fundamentals of Carbanion Chemistry"; Academic Press: New York, 1965. (b) Dart, E. C. "Reactivity, Mechanism and Structure in Polymer Chemistry"; Jenkins, A. D., Ledwith, A., Eds.; Wiley: New York, 1974; Chapter 10. (c) Schlosser, M. "Struktur und Reaktivität Polarer Organometalle"; Springer-Verlag: West Berlin, 1973; p 87 et seq. (d) Lambert, J. B. *Top. Stereochem.* 1971, 6, 19. (e) Lehn, J. M. *Fortschr. Chem. Forsch.* 1970, 14, 311. (f) Rauk, A.; Allen, L. C.; Mislow, K. *Angew. Chem., Int. Ed. Engl.* 1970, 9, 400. (g) Peoples, P. R.; Trainor, T. M.; Grutzner, J. B. "Stereochemistry in Molecular Systems"; Sarma, R. H., Ed.; Pergamon Press: New York, 1979; p 131.

(2) (a) Köbrich, G.; Merkel, D.; Imkamp, K. *Chem. Ber.* 1973, 106, 2017. (b) Ratajczak, A.; Anet, F. A. L.; Cram, D. J. *J. Am. Chem. Soc.* 1967, 89, 2072.

(3) (a) Sutherland, I. O. *Annu. Rep. NMR Spectrosc.* 1971, 4, 71. (b) Jackman, L. M.; Cotton, F. A. "Dynamic Nuclear Magnetic Resonance Spectroscopy"; Academic Press: New York, 1975.

(4) Peoples, P. R. Ph.D. Thesis, Purdue University, 1979 (provides detailed experimental procedures and spectral information).

(5) Gassman, P. G.; Marshall, J. L. *Org. Synth.* 1968, 48, 25.

(6) Jung, M. E., private communication.

(7) It is important that the tetrachloro ketal solution be homogeneous. The rate of addition is not critical. The only result of too rapid a rate of addition is that the ammonia will reflux.

(8) Clark, F. R. S.; Warkentin, J. *Can. J. Chem.* 1971, 49, 2223.

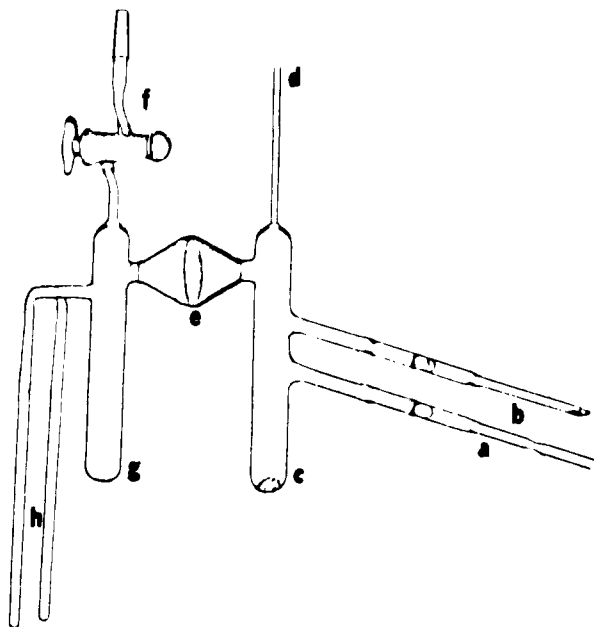


Figure 1. Apparatus for generation of anion samples.

respectively, was obtained in 81% yield. 7-Hydroxy-7-phenylnorbornene (38.3 g, 0.206 mol) dissolved in THF (300 mL) in a flame-dried 1-L flask was cooled to 0 °C. Sodium hydride (5.43 g, 0.226 mol) was added slowly, the mixture stirred for 0.5 h, methyl iodide (14.2 mL, 32.1 g, 0.226 mol) added via syringe, and the reaction stirred at room temperature for 20 h. Ethanol quench, pentane workup, and vacuum distillation (108 °C (4 mm)) gave a 3.2:1 mixture of *syn*- and *anti*-7-phenyl-7-methoxynorbornenes (33.7 g, 82% yield) as a colorless oil.

<sup>13</sup>C NMR (CDCl<sub>3</sub>): 139.02 (s), 132.39 (d), 128.07 (d), 127.53 (d), 127.40 (d), 98.84 (s), 52.83 (q), 46.10 (d), 22.46 (t) for *syn*; 139.78 (s), 134.40 (d), 129.21 (d), 128.71 (d), 126.75 (d), 97.70 (s), 51.05 (q), 46.78 (d), 23.55 (t) for *anti*.

In a flame-dried, 300 mL, three-necked round-bottomed flask were placed the epimeric ethers (11.0 g, 54.9 mmol), anhydrous ethyl acetate (100 mL), and 10% palladium on charcoal catalyst (0.231 g). Hydrogen gas was bubbled through this solution, with the aid of a gas dispersion tube, until TLC (CH<sub>2</sub>Cl<sub>2</sub>) indicated no more starting material was present (ca. 7 h). The reaction mixture was filtered through a Celite plug rinsed with ethyl acetate (50 mL) and solvent removed in vacuo followed by vacuum pump drying to give an opaque oil (11.50 g, 95% yield). Vacuum sublimation (0.1 mm) at room temperature gave 7-phenyl-7-methoxynorbornane as a pale white solid (mp 31.5–32 °C).

IR (neat): 2941, 2793, 1445, 1332, 1236, 1131, 1081, 762, 695. <sup>1</sup>H NMR (CDCl<sub>3</sub>) (100 MHz): 7.60–7.23 (m, 5 H), 2.95 (s, 3 H), 2.54 (m, 2 H), 2.30–1.95 (m, 2 H), 1.70–1.05 (complex, 6 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 139.96 (s), 128.62 (d), 127.62 (d), 127.38 (d), 92.72 (s), 51.71 (q), 40.07 (d), 28.60 (t), 27.21 (t).

An alternate sequence involving double-bond reduction prior to deketalization was less productive.

**Solvents for Anion Preparation.** THF (Baker or Mallinckrodt reagent grade) was predried over molecular sieves (Linde 4A) or sodium ribbon followed by distillation from sodium benzophenone ketyl or lithium aluminum hydride (LAH) in an analytical still, under nitrogen. DME (Ansol 121) was treated similarly before use. THF-*d*<sub>8</sub> (Merck Sharp and Dohme, 99.8 atom % D) and DME-*d*<sub>10</sub> (Merck Sharp and Dohme, 99 atom % D) were stored over LAH. The solvent was placed in a flask containing LAH, the flask was connected to the vacuum line, and the solution was frozen in liquid nitrogen. The solvent was degassed by the freeze-pump-thaw technique five times. The solvent was stored over LAH under vacuum prior to transfer to the anion generation apparatus by direct vacuum distillation.

**(7-Phenylnorbornyl)potassium.** The anion generation procedure evolved from the basic method of Winstein.<sup>10</sup> Sublimed 7-phenyl-7-methoxynorbornane (200 mg, 1 mmol) was sealed into side arm a of the apparatus, shown in Figure 1, under high vacuum. The tube was cooled with either crushed dry ice or liquid nitrogen during this process to prevent vaporization or thermal decomposition. For preparation of the

lithium compound, anhydrous lithium bromide was also sealed into side arm b in an analogous manner but without cooling. A magnetic stirring bar and iron breaker were remotely located in the pocket provided by frit e. The thoroughly cleaned apparatus was flamed out under vacuum and a final check for leaks made. The vacuum was broken and nitrogen passed through the apparatus. Sodium/potassium alloy (0.5 mL) was transferred by dry syringe (2 mL, 20 gauge needle) to reaction chamber c via the stoppered port d. The apparatus was then connected to the high vacuum line by way of stopcock f and port d sealed off under vacuum. The apparatus was evacuated to less than 10<sup>-5</sup> torr while being flame dried several times. The pressure was measured with a McLeod gauge (Kontes, Model 923500-25).

THF was distilled into the apparatus, under vacuum, by cooling reaction chamber c with liquid nitrogen. Once the desired volume of solvent (15–25 mL) had been distilled, stopcock f was closed, and the apparatus was removed from the vacuum line. The solvent and alloy were allowed to warm until the alloy melted (ca. –5 °C) with chamber c immersed in an ice-salt bath. They were stirred together for 30–60 min, and the characteristic blue color of the solvated electron appeared.<sup>11</sup> The break-seal in side arm a was now broken with the aid of the iron breaker manipulated with an external magnet. The methyl ether was washed into the cool reaction chamber by repeatedly tipping the apparatus. A faint red color was observed almost immediately on the alloy surface upon contact with the ether which deepens to a dark crimson within 60 s.<sup>11</sup> This solution was stirred vigorously for ca. 1 h at –10 to –5 °C. The anion solution was now filtered, to remove unreacted alloy and metal salts, through frit e (Ace Glass, porosity C, 25–50 μm). This filtration process was generally carried out in the temperature range –50 to –40 °C and typically required 30–90 min. The entire apparatus was immersed in an ethanol bath which was maintained at low temperature by a recirculating cooler (Neslab LT-9). Once the filtration process was completed, the solution was concentrated in the NMR sample tubes h by immersing chamber g into a Dewar of liquid nitrogen and back-distilling solvent. A sample of the anion in THF was sealed off at liquid-nitrogen temperature.

If the anion was to be studied in THF-*d*<sub>8</sub> or DME-*d*<sub>10</sub> the apparatus was reconnected to the vacuum line, making sure that the connecting port area was again flame dried and the system was down to pressure. Stopcock f was opened and solvent distilled out of the apparatus into a receiver cooled in liquid nitrogen on another part of the vacuum line. Once all the solvent was removed, the apparatus was opened to the main vacuum and any unreacted starting material or quenched hydrocarbon sublimed away. The sublimation step was generally carried out at 0 °C for 1–2 h. The desired solvent was now distilled in, and the 8- or 12-mm NMR tubes were sealed at liquid-nitrogen temperature. All anion samples, once sealed, were stored in a Dewar at –78 °C. During the sublimation process, solid samples of the potassium salt of the 7-phenylnorbornyl carbanion appeared as red to bright orange crystals on the inner surfaces of the apparatus.

**(7-Phenylnorbornyl)cesium** was prepared by simply replacing the Na/K alloy in the above procedure with Cs/Na/K alloy<sup>12</sup> (MSA Research Corp.; 40% Cs, 48% K). The ether cleavage may be performed at –40 °C with this low melting alloy.

**(7-Phenylnorbornyl)lithium** was prepared by a metathesis reaction<sup>13</sup> with anhydrous lithium bromide. Anhydrous lithium bromide (MCB reagent) was placed in a round-bottom flask and evacuated on the vacuum line with external flaming to 10<sup>-5</sup> torr. Sufficient anhydrous THF was distilled under vacuum to dissolve the solid. The salt was stirred for 30 min followed by removal of THF under high vacuum. The deposited salt was then heated at 150 °C under vacuum for 12 h, and the entire process was repeated two more times. After the third cycle the lithium bromide was heated at ca. 200 °C for 2 days. The flask was sealed via the vacuum stopcock and stored in a glovebag under argon. Samples for anion work were transferred to break-seal tubes with vacuum flame-dried equipment under argon. They were isolated by vacuum stopcock and sealed off immediately under high vacuum. This anhydrous salt is extremely sensitive to moisture.

A THF solution of the potassium compound was prepared according to the above procedure. After being stirred over the alloy for 1 h, the solution was cooled to –25 °C.<sup>14</sup> The break-seal b was broken and lithium bromide (175 mg) added. The mixture was stirred for 30 min and filtered to remove alloy and insoluble salts at ca. –45 °C, and an

(9) The major *syn* isomer has the hydroxyl group *syn* to the double bond.

(10) Winstein, S.; Ogliaruso, M.; Sakai, M.; Nicholson, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 3656.

(11) Color development provides an indication of material purity. Impure materials will show considerable variation in the time and shade of color development.

(12) Grovenstein, E., Jr.; Rhee, J. U. *J. Am. Chem. Soc.* **1975**, *97*, 769.

(13) Schlosser, M.; Hartmann, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 508.

(14) The dissolution of LiBr in THF is highly exothermic.

Table I. Cation Composition of NMR Samples (%)<sup>a</sup>

| cation source                  | Li <sup>+</sup> | Na <sup>+</sup> | K <sup>+</sup> | Cs <sup>+</sup> |
|--------------------------------|-----------------|-----------------|----------------|-----------------|
| Na/K alloy                     | 0.0             | 0.7             | 97.5           | 1.8             |
| Cs/Na/K alloy                  | 0.0             | 0.1             | 0.1            | 99.8            |
| Na/K alloy + LiBr <sup>b</sup> | 56.8            | 0.9             | 40.4           | 1.9             |
| Na/K alloy + LiCl              | 1.0             | 0.7             | 98.3           | ...             |

<sup>a</sup> Atomic emission analysis of samples of 7-phenylnorbornanide ion prepared from cation source shown after water quench. A background correction has been applied and experimental error is  $\pm 2\%$ . <sup>b</sup> This sample was used for the exchange study.

NMR sample was sealed. The sample in THF-*d*<sub>8</sub> was prepared analogously. The THF solvent was removed after filtration to give a bright yellow solid, the deuterated solvent (ca. 5 mL) was distilled onto the yellow solid, and an NMR sample was sealed. The NMR experiments were performed over a 4-week period, and the sample was stored at  $-78^\circ\text{C}$  between experiments. The only detectable change in the  $^{13}\text{C}$  spectrum was the slow diminution of anion peaks and growth of hydrocarbon peaks. After the NMR studies had been completed, the sample concentration was estimated by comparing the integrated intensity of the anion spectrum with the intensity of a standard sample which was substituted for the anion sample. The concentration of anion ( $0.05 \pm 0.01$  M) and hydrocarbon ( $0.03 \pm 0.01$  M) were determined by integration of the CW proton spectrum against a standard solution of bromobenzene in THF (1 M). The lithium concentration was estimated to be  $2.6 \pm 0.5$  M by integration of the 38.9-MHz lithium FT spectrum against a standard solution of LiBr in THF (1M).

The metathesis reaction failed when anhydrous lithium chloride was substituted for the bromide. Only the spectrum of the potassium salt was detected, and atomic emission analysis showed only 10% lithium incorporation. It is worth noting that no peaks attributable to methoxide ion were detected in any spectra.

**Cation Analysis.** The cation composition of the NMR samples was determined by atomic emission analysis, using the technique and instrumentation developed by Pardue.<sup>15</sup> Samples for analysis were prepared by quenching anion samples with water (10 mL) followed by ether extraction ( $3 \times 20$  mL) to remove organics. The aqueous extract was diluted with an equal volume of a standard rubidium solution (100 mg/L) which functions as an ionization buffer and serves to enhance sensitivity. This solution was then diluted to an appropriate volume to bring the ion concentration into a range of linear response. The results are shown in Table I.

**Anion Quench.** In one experiment, a single NMR sample of 7-phenylnorbornylpotassium was prepared according to the above procedure. The sample was quenched by pouring into methanol (10 mL) which had been deoxygenated by bubbling with nitrogen for 15 min. The methanol mixture was extracted with pentane, the volume reduced to ca. 1 mL by evaporation, and the 7-phenylnorbornane analyzed by GC. A 55% yield was obtained on the basis of the starting methyl ether. Loss of material due to incomplete filtration after anion generation was common.

During the course of this investigation, several qualitative observations have been made concerning the lifetime of anions in ether solvents. Although sealed anion samples may be stored for extended periods of time (on the order of 2 months) provided they are maintained at  $-78^\circ\text{C}$  or below, warming to room temperature for 30–60 min resulted in sufficient decomposition to render the sample useless for further  $^{13}\text{C}$  investigation. DME was found to react faster than THF and is reactive enough to prevent preparation of an anion in this solvent.<sup>16</sup> As noted earlier, samples desired in DME are first prepared in THF followed by solvent exchange at low temperature.

It appeared reasonable that solvent deprotonation was responsible for anion decomposition. In addition to the obvious advantage of deuterated solvents for  $^{13}\text{C}$  studies, THF-*d*<sub>8</sub> and DME-*d*<sub>10</sub> were used as solvents since the rate of decomposition in these solvents was slower due to the kinetic isotope effect of deuterium. Several samples were purposely allowed to warm to room temperature in the deuterated solvents and the products examined by  $^{13}\text{C}$  NMR spectroscopy. The only spectrum observed was that of 7-phenylnorbornane. Remarkably there was no evidence of significant D incorporation at C7 or any other position. The spectrum was indistinguishable (within  $\pm 10\%$  peak-height variation) from that of authentic 7-phenylnorbornane. No other species were detected in the spectrum. In one instance, hydrocarbon from a decomposed anion sample was purified by preparative GC and analyzed by high-resolution mass

spectrometry. The results showed  $11 \pm 2\%$  deuterium incorporation.  $^{13}\text{C}$  NMR analysis of the proton content of the solvent in a case where the greatest amount of residual protonated THF was present showed a D/H ratio of at least 2:1. Anion quench by solvent thus shows an isotope effect of at least 10. A detailed study of the source of these unusual observations is planned.

**Carbon NMR spectra** were obtained on a Nicolet NT-150 spectrometer operating in the Fourier transform mode at 37.735 MHz. Data handling was performed on a Nicolet 1180 computer employing program 80502. Broad band proton decoupling was accomplished with 100-Hz square wave modulation which gave efficient decoupling over 7 kHz. The decoupler was centered at  $\delta$  2.6 in the proton spectrum. The deuterium signal from the solvent THF-*d*<sub>8</sub> provided the field frequency lock. Chemical shifts ( $\delta$ ) were calculated from the shift of the internal THF resonance assumed to be 26.00 ppm. The instrumental parameters for data collection were as follows:  $90^\circ$  excitation pulse (24  $\mu\text{s}$ ), acquisition delay (125  $\mu\text{s}$ ), quadrature phase detection with a  $\pm 4000$  Hz spectral window, 16K data points, no pulse delay, and exponential weighting to produce a 1 Hz line width. With broad lines a 2-Hz exponential weighting was used. The number of accumulations varied from 4000 to 10000 depending on signal/noise and line width considerations.

Temperature control was provided by a countercurrent flow of pre-cooled nitrogen gas by using the Nicolet variable-temperature control unit (VTCU) supplied with the instrument. The temperature is set and regulated under software control and protected with manual overrides. A continuous LED temperature display was provided through a thermocouple located immediately beneath the sample. The thermocouple was precalibrated by using the frequency difference between the signals in methanol.<sup>17</sup> A calibration check at  $-90^\circ\text{C}$  was made when the proton spectrum of methanol was obtained by interchanging observe and decoupler channels and reshimming the magnet. This procedure was time consuming and was therefore not repeated at other temperatures. The indicated temperature was found to be within  $1^\circ\text{C}$  of that measured from the methanol spectrum. At each new temperature the spectrometer was allowed to equilibrate for a minimum of 20 min before data acquisition was begun. The absolute temperature is estimated to be accurate to  $\pm 2^\circ\text{C}$ . The lower limit of  $-90^\circ\text{C}$  was set by instrumental considerations and the upper limit of  $-30^\circ\text{C}$  by sample stability.

Additional experiments were performed on a Varian XL-100 spectrometer operating at 25.16 MHz and an NT-360 spectrometer operating at 90.54 MHz. The spectral parameters were equivalent to those used above. The temperature on the XL-100 was maintained with a V-4341 controller. Temperature was measured with a thermocouple immersed in THF. The data were less reliable because of poorer signal/noise ratio, but the results were in good agreement with those obtained at 37 MHz. An experiment at 90 MHz was attempted to determine the coalescence temperature. At such high magnetic field strengths the proton chemical shifts are so dispersed that high decoupler power is required to decouple all protons from carbon. The high power levels, in turn, cause sample-heating problems. Therefore, single frequency proton-decoupled carbon spectra were obtained over the temperature range  $-40$  to  $-65^\circ\text{C}$ .

The coalescence temperature at 90 MHz was found to be  $-50 \pm 5^\circ\text{C}$ . However, substantial temperature variations were observed as a result of decoupler heating effects. This observation was established in a separate experiment. A  $^{13}\text{C}$  thermometer<sup>18</sup> consisting of a 50/50% v/v mixture of acetone-*d*<sub>6</sub> and carbon tetrachloride was employed in an inner 8-mm NMR tube. The temperature was indicated by the chemical shift difference,  $\Delta\delta$ , between the acetone carbonyl carbon and carbon tetrachloride. Equation 1 is a modification, for the NT-360, of the equation

$$T = 5529.1 - 50.734(\Delta\delta) \quad (1)$$

described by Led and Petersen.<sup>18</sup> The 8-mm NMR tube was placed coaxially in a 12-mm tube and the outer annulus filled with either neat THF or a solution containing lithium bromide in THF (ca. 1 M) chosen to simulate a lithium anion sample. This arrangement was used to measure the temperature with and without decoupler power applied. The temperatures observed were  $-80$  (decoupler off),  $-70$  (decoupler on, THF sample), and  $-52^\circ\text{C}$  (decoupler on, lithium bromide sample). This variation of temperature with sample and decoupler power accounts for the large experimental error for the coalescence temperature measured at 90 MHz.

#### Data Analysis

All line shape calculations were performed on a CDC 6500 computer using the McConnell equation<sup>19</sup> incorporated in a two-site line shape

(15) Felkel, H. L.; Pardue, H. L. *Anal. Chem.* **1978**, *50*, 602.

(16) Moncur, M. V.; Grutzner, J. B. *J. Am. Chem. Soc.* **1973**, *95*, 6449.

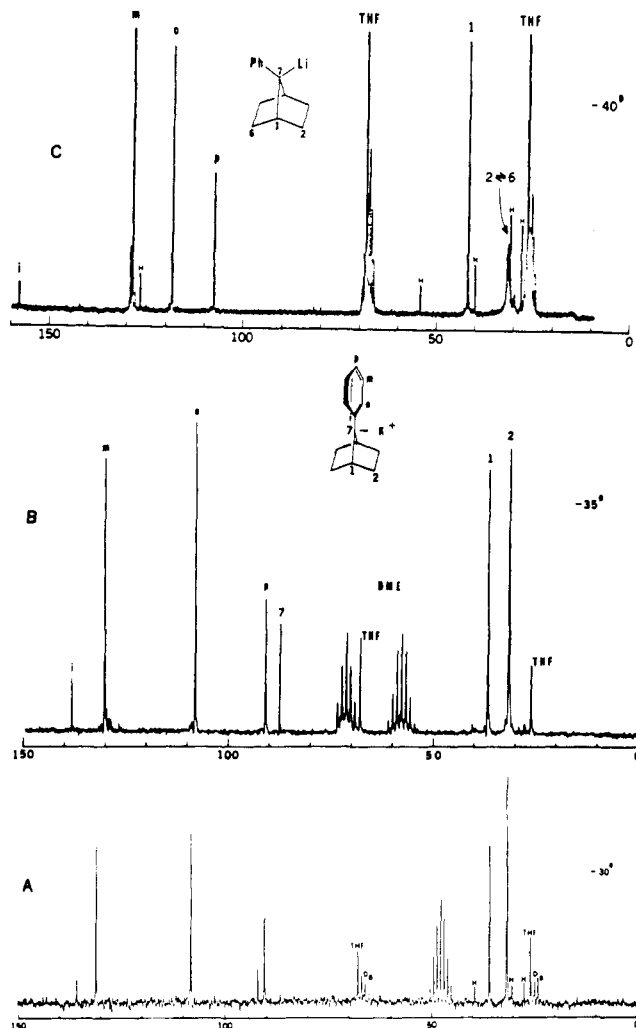
(17) (a) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227. (b) Van Geet, A. L. *Ibid.* **1970**, *42*, 679.

(18) Led, J. L.; Petersen, S. B. *J. Magn. Reson.* **1978**, *32*, 1.

**Table II.** Carbon-13 and Proton NMR Chemical Shifts of 7-Phenylnorbornyl Alkali as a Function of Cation and Temperature<sup>a</sup>

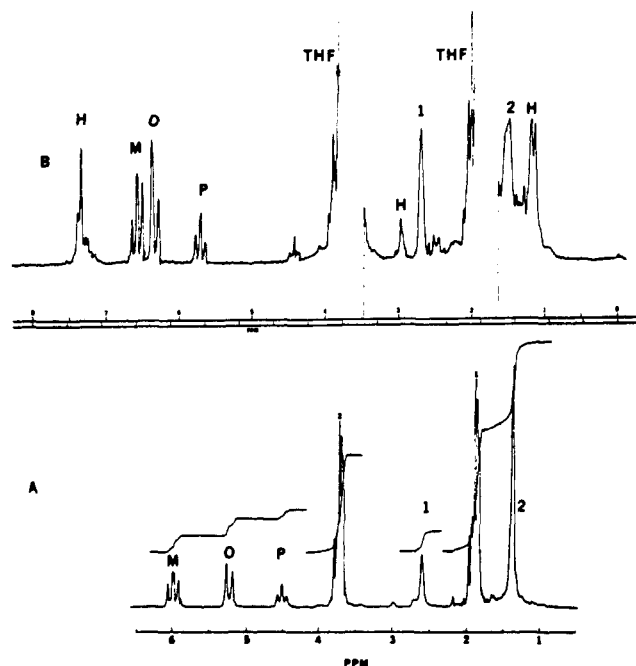
| temp,<br>°C | cation           | C <sub>i</sub> | C <sub>m</sub> (H) <sup>b</sup> | C <sub>o</sub> (H) | C <sub>p</sub> (H) | C7    | C1,4 (H)    | C(anti) | C(syn) |
|-------------|------------------|----------------|---------------------------------|--------------------|--------------------|-------|-------------|---------|--------|
| -30         | Cs <sup>+</sup>  | 136.0          | 131.2 (5.86)                    | 108.2 (5.09)       | 90.4 (4.38)        | 91.8  | 36.0 (2.58) | 31.7    | 31.7   |
| -60         | Cs <sup>+</sup>  | 136.2          | 131.3                           | 108.3              | 90.5               | 91.4  | 36.0        | 31.7    | 31.7   |
| -90         | Cs <sup>+</sup>  | 136.4          | 131.7                           | 108.3              | 90.5               | 91.4  | 36.1        | 31.7    | 31.7   |
| -30         | K <sup>+</sup>   | 137.7          | 129.8 (5.90) <sup>c</sup>       | 107.6 (5.23)       | 90.9 (4.37)        | 88.1  | 36.6 (2.5)  | 31.4    | 31.4   |
| -60         | K <sup>+</sup>   | 137.4          | 129.6                           | 107.6              | 90.6               | 88.1  | 36.5        | 31.4    | 31.4   |
| -90         | K <sup>+</sup>   | 137.0          | 129.4                           | 107.5              | 90.1               | 88.1  | 36.5        | 31.4    | 31.4   |
| -30         | Li <sup>+</sup>  | 157.3          | 128.0                           | 117.8              | 107.1              | 64.3  | 41.5        | 31.0    | 31.0   |
| -60         | Li <sup>+</sup>  | 157.2          | 128.0 (6.49)                    | 117.7 (6.24)       | 107.0 (5.62)       | 64.3  | 41.4 (2.63) | 31.0    | 31.0   |
| -90         | Li <sup>+</sup>  | 157.1          | 128.0                           | 117.6              | 106.8              | 64.3  | 41.3        | 33.2    | 28.8   |
| <i>d</i>    | H                | 141.9          | 128.6                           | 128.3              | 126.1              | 54.2  | 40.1        | 30.9    | 27.9   |
| <i>e</i>    | OCH <sub>3</sub> | 139.96         | 128.62                          | 127.62             | 127.38             | 92.72 | 40.07       | 28.60   | 27.21  |

<sup>a</sup> Upfield resonance of THF set equal to 26.00 ppm. <sup>b</sup> Proton resonances are shown in parentheses. <sup>c</sup> In DME-*d*<sub>10</sub> at -45 °C. <sup>d</sup> Data for 7-phenylnorbornane in THF at probe temperature. <sup>e</sup> 7-Methoxy-7-phenylnorbornane in CDCl<sub>3</sub>.



**Figure 2.** The carbon-13 NMR spectra of alkali 7-phenylnorbornanides. Peaks labeled H are hydrocarbon: (A) cesium salt at -30 °C in THF-*d*<sub>8</sub>; (B) potassium salt at -35 °C in DME-*d*<sub>10</sub>; (C) lithium compound at -40 °C in THF-*d*<sub>8</sub>. The peak for C7 (64.3 ppm) has been lost in the noise because of insufficient pulse delay. The multiplet at 48 ppm is from the external lock, MeOH-*d*<sub>4</sub>.

exchange program provided by Dr. J. Lambert of Northwestern University. The line width in the absence of exchange was taken to be the half-height line width of the solvent peaks. The maximum separation for the frozen form was taken as 167 Hz measured at -90 °C. No correction for the temperature dependence of the chemical shifts was applied. The average chemical shift at -30 °C was  $\delta$  30.99 which is in agreement with the mean of the low-temperature values of 28.77 and 33.21 ppm. That



**Figure 3.** The 100-MHz proton NMR spectra of alkali 7-phenylnorbornanides in THF-*d*<sub>8</sub>: (A) cesium salt at -30 °C; (B) lithium compound at -50 °C (H = hydrocarbon, THF = solvent).

these were the limiting shifts in the frozen form could normally be checked by going to lower temperature. However, this was not possible due to instrumental limitations. Upon going from -80 to -90 °C we observed the separation to increase by only 4.5 Hz over the 10 °C range, an increase of <3%. Such an increase in peak separation would be expected if the exchange process had not been slowed sufficiently at -80 °C to obtain the frozen spectrum. The separation of peak maxima in the simulated spectrum at -80 °C was calculated to be 5 Hz less than the true chemical shift difference used as input data.

Simulated spectra were calculated for a range of  $\tau$  values and scaled so that the calculated line maxima agreed with the peak-height maxima in the experimental spectra. The rate constants,  $\tau^{-1}$ , were estimated for each temperature by visual comparison of the experimental and calculated spectrum. The error limits were defined by taking the closest value on either side of the best fit value for which the visual fit was obviously unacceptable. This method resulted in errors in the rate constants as large as 50% at the temperature extremes. The thermodynamic quantities were derived from a van't Hoff plot of  $\ln(k/T)$  vs.  $1/T$ . The error limits on the data points were estimated by comparison of observed and calculated spectra. The best-fit straight line was obtained by least-squares analysis. The errors in the slope and intercept (and thus  $\Delta H^\circ$  and  $\Delta S^\circ$ ) were estimated by constructing straight lines of maximum and minimum slope which passed through the limits of the error bars. This method of error estimation is more realistic than a simple statistical approach because the points at the extremes of the plot are considered individually. These points are both the most error prone and the most significant in the determination of slope and intercept.<sup>20</sup>

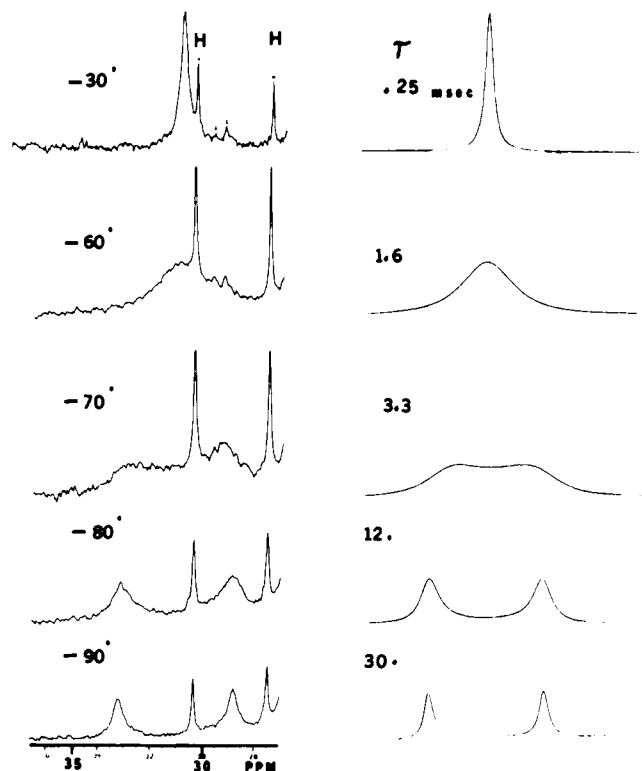
(19) (a) McConnell, H. M. *J. Chem. Phys.* **1958**, *28*, 430. (b) Reference 3a.

(20) Binsch, G., in ref 3b, Chapter 3.

**Table III.** Activation Energy Data for Pyramidal Inversion in (7-Phenylnorbornyl)lithium in THF-*d*<sub>8</sub> (~0.05 M) from Line Shape Analysis of C2-C6 Exchange in <sup>13</sup>C NMR Spectrum

| frequency,<br>MHz | <i>T</i> <sub>c</sub> , °C | <i>k</i> <sub>c</sub> , s <sup>-1</sup> | Δ <i>G</i> <sub>c</sub> <sup>‡</sup> , <sup>a</sup><br>kcal/mol | Δ <i>H</i> <sup>‡</sup> , <sup>b</sup><br>kcal/mol | Δ <i>S</i> <sup>‡</sup> , <sup>b</sup><br>gibbs | Δ <i>G</i> <sup>‡</sup> , <sup>b</sup><br>kcal/mol |
|-------------------|----------------------------|-----------------------------------------|-----------------------------------------------------------------|----------------------------------------------------|-------------------------------------------------|----------------------------------------------------|
| 25.2              | -84 ± 2                    | 247 ± 5                                 | 8.8 ± 0.2                                                       | 6.4 ± 3                                            | -13 ± 14                                        | 8.9 ± 5                                            |
| 37.7              | -68 ± 2                    | 371 ± 5                                 | 9.4 ± 0.2                                                       | 6.7 ± 2                                            | -14 ± 10                                        | 9.6 ± 3                                            |
| 90.5              | -50 ± 5                    | 891 ± 11                                | 9.9 ± 0.3                                                       |                                                    |                                                 |                                                    |

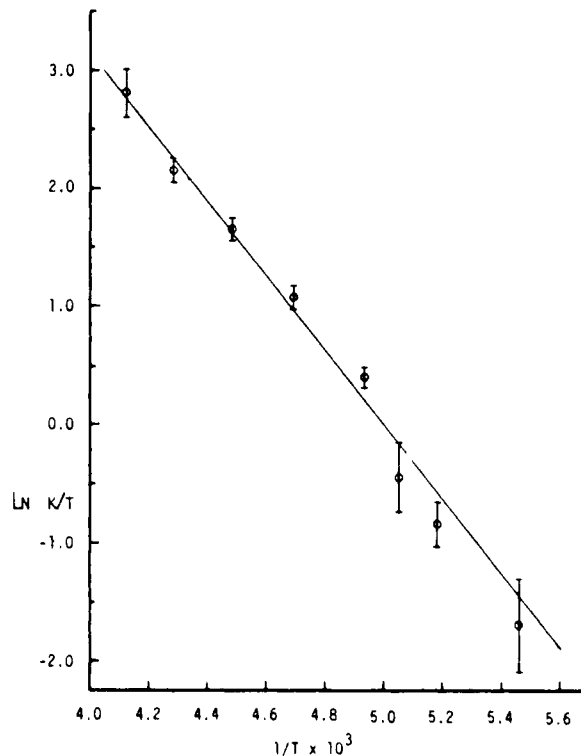
<sup>a</sup> Rate (*k*<sub>c</sub>) at coalescence temperature (*T*<sub>c</sub>) and Δ*G*<sub>c</sub><sup>‡</sup>. See Experimental Section. <sup>b</sup> Activation energies derived from slope and intercept of van't Hoff plot and Δ*G*<sup>‡</sup> = Δ*H*<sup>‡</sup> - *T*<sub>c</sub>Δ*S*<sup>‡</sup>.

**Figure 4.** The high-field region of the carbon NMR spectrum of lithium 7-phenylnorbornanide as a function of temperature (°C). Calculated spectra and lifetimes (τ, ms) are shown on the right (H = hydrocarbon, X = unknown impurity).

The rate constant (*k*<sub>c</sub>) at the coalescence temperature (*T*<sub>c</sub>) was estimated from the equation  $k_c = \pi(\Delta\nu)/2^{1/2}$  where Δν is the chemical shift difference between the peaks in the slow-exchange spectrum (167 Hz, -90 °C). The activation free energy (Δ*G*<sub>c</sub><sup>‡</sup>) was then calculated from  $k_c = (kT_c/h) \exp(-\Delta G_c^\ddagger/RT_c)$ .

## Results

Carbon-13 and proton NMR spectra of (7-phenylnorbornyl)-cesium, -potassium, and -lithium are shown in Figures 2 and 3. Peak assignments and chemical shifts are shown in Table II. The spectra of the cesium and potassium salts are similar in both THF and DME and only show minor changes with temperature in the range -30 to -90 °C. The chemical shifts in the aromatic region are typical of delocalized benzylic anions.<sup>21,22</sup> The ortho and, particularly, the para resonances show significant upfield shifts, and the meta resonance is shifted to a smaller extent from the neutral value. The multiplet structure in the proton spectra is characteristic of monosubstituted aromatics. The high-field region of the carbon spectrum contains the critical structural information. Only 2 peaks assigned to the aliphatic carbons of the anion are observed at all temperatures down to -90 °C (-105 °C at 25

**Figure 5.** van't Hoff plot (ln (*k*/*T*) vs. 1/*T*) of the exchange rate constant (*k*, s<sup>-1</sup>) for pyramidal inversion in (7-phenylnorbornyl)lithium in THF-*d*<sub>8</sub> as a function of (*T*, K).

MHz) for the cesium and potassium compounds.<sup>23</sup>

The chemical shifts and temperature dependence of the spectra of (7-phenylnorbornyl)lithium are dramatically different. The most obvious change occurs for C7 and the para carbon. In the potassium and cesium derivatives, these peaks are almost overlapped whereas they differ by over 30 ppm in the lithium compound. Less obvious, but equally dramatic shifts occur at the ipso carbon (20 ppm) and C1 (5 ppm). This shift of the bridgehead position is unprecedented and strongly suggests a change of structure of the carbon skeleton. As the sample is cooled, the shifts are almost unchanged, but the C2 resonance broadens and eventually splits into two discrete signals (C2 and C6) (Figure 4). The changes are reversible with temperature and show typical coalescence phenomena consistent with inversion of a pyramidal system with a time constant comparable to the NMR time scale.

A line shape analysis of the two-site exchange process was undertaken at 37.7 MHz.<sup>24</sup> The van't Hoff plot of the exchange rate as a function of temperature is shown in Figure 5. The derived thermodynamic parameters are shown in Table III. The relatively large negative activation entropy was noted. Because of the notoriously large errors associated with entropies derived

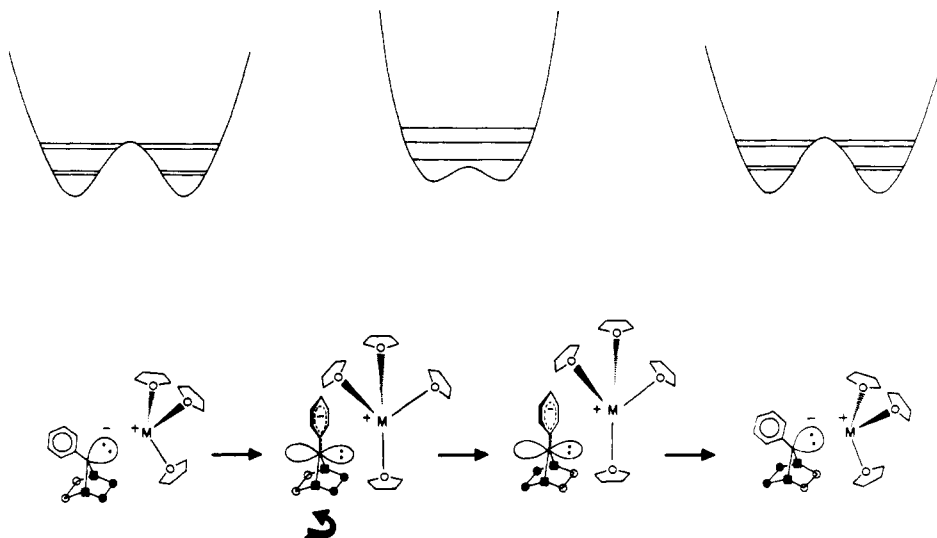
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(23) At low temperature (-90 °C) selective line broadening of anion peaks occurs relative to solvent and hydrocarbon signals. The broadening which is present for all anion peaks is tentatively attributed to a T<sub>2</sub> phenomenon arising from anion association. Details may be found in ref 4, and a spectrum has been published.<sup>18</sup>

(24) Line shape analysis was also undertaken at 25.2 MHz but was less reliable because of poor signal/noise.

Scheme I



by NMR methods,<sup>20</sup> a check of the temperature dependence of  $\Delta G^\ddagger$  was made. This may be accomplished by determining the coalescence temperature as a function of field strength.<sup>25</sup> While uncertainties in the temperature measurement at 90.5 MHz prevented quantitative analysis, the fact that  $\Delta G^\ddagger$  increased significantly with temperature over a 35 °C range requires that the entropy of activation be large and negative. While detailed studies of concentration effects were not undertaken, exchange rates determined for samples which differed by a factor of 3 in concentration were the same within experimental error.

## Discussion

**Interpretation of Results.** The following conclusions may be drawn from the results. (7-Phenylnorbornyl)lithium is pyramidal in THF (structure I<sub>B</sub>) with a barrier to inversion at 25 °C of  $11 \pm 1$  kcal/mol (obtained by extrapolating the coalescence data). The structure of the organic skeleton is strongly dependent on the choice of metal ion. It is our interpretation that (7-phenylnorbornyl)potassium and -cesium have a planar structure (I<sub>A</sub>). This is based on the belief that the chemical shift changes between the lithium and potassium compounds are so large that only a fundamental change in structure could be responsible. The unanticipated shift change at the bridgehead carbon is particularly striking. It should also be noted that if the observed chemical shifts for the potassium species should prove to be the time average of a rapidly inverting structural pair, the limiting value for the chemical shift difference between the pyramidal organolithium and a planar ion will be even greater. To our knowledge, this is the first example where the average chemical shifts for an equilibrating pair of species is not equal to the shift of the intermediate species. Correlation of carbon chemical shifts with charge density is particularly dangerous when a structure change is involved.<sup>26</sup> However, Fraenkel<sup>27</sup> has shown that for para carbon shifts in aromatic systems, the charge and bond contributions to the shift are parallel and approximately equal. Thus the large downfield shift observed at the para position indicates that the electron density is significantly diminished at that position in the lithium derivative. The direction of the shift changes at the ortho, ipso, and C7 carbons is also consistent with charge localization and pyramidalization at C7 in the lithium derivative relative to the potassium analogue.

The critical dependence of carbon structure on counterion and the significantly negative entropy of activation show that the process being detected is not simple anion inversion. It is well

established that even delocalized carbanions exist as ion pairs in ether solvents.<sup>28</sup> In fact, all available evidence is that benzylic anions are coordinated as tightly as contact ion pairs under our experimental conditions and the question of whether even greater covalency is involved in benzylic lithium species remains to be settled.<sup>29</sup> Simple anion inversion would be expected to have a small activation entropy ( $\sim 2$  gibbs) corresponding to the loss of a single vibrational degree of freedom in passing from the pyramidal to planar structure.<sup>30</sup> The large value obtained here, although lamentably inaccurate, clearly demands greater organization during the interconversion. In fact, the sign and magnitude of the activation enthalpy and entropy are comparable to the equilibrium thermodynamic quantities determined for ion-pair dissociation processes.<sup>28,31</sup> The conclusion is that solvation of the cation is the rate-determining step in these processes and not anion inversion per se. The following model is proposed to account for the observations (Scheme I).

It is our contention that the 7-phenylnorbornyl anion is intrinsically planar. When this anion is coordinated to the strongly polarizing lithium cation, the Coulombic stabilization increases the electron localization at C7. The formation of a tetracoordinate carbon and the greater stabilization available to s electrons combine to convert the planar-delocalized anion into a pyramidal organolithium.

The state of aggregation in these solutions has not been determined. For simplicity, the inversion process has been treated as if it were unimolecular (including the solvent shell and cation of course). On the basis of the selective line broadening observed for the potassium derivative at low temperature<sup>23</sup> relative to hydrocarbon lines, one may speculate that the bulk of the solution is composed of higher aggregates. The dielectric heating by the decoupler shows that ionic species are present. A lithium NMR spectrum (38 MHz) taken on a sample used for inversion studies shows two distinct resonances at  $-50$  °C: a broad ( $\sim 80$  Hz) low-intensity peak at low field and a strong sharp signal which can be assigned to lithium bromide. Exchange between lithium bromide and the organolithium is slow on the NMR time scale ( $< 100$  s<sup>-1</sup>). Thus these observations indicate that monomers may not be the predominant species in solution. Our conclusion that

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the 7-phenylnorbornyl carbanion is planar is not affected.

**The Inversion Barrier in Carbanions.** A detailed discussion of carbanion inversion processes has recently been published,<sup>18</sup> so only a brief summary of the conclusions will be included here. Theoretical<sup>32</sup> and experimental<sup>33</sup> estimates agree that methyl anion in the gas phase is pyramidal with an inversion barrier of 2 kcal/mol or less. They differ on the sign of the electron affinity. In the solid state, methylolithium and methylpotassium are pyramidal<sup>34</sup> and benzylolithium is unsymmetrical.<sup>29a</sup> Monomeric methylolithium in an argon matrix is pyramidal<sup>35</sup> with an out-of-plane bending frequency of 1158 cm<sup>-1</sup>. In solution, simple aliphatic carbanions have been generated which invert more rapidly than they are protonated by the relatively acidic solvents water<sup>36</sup> and dimethyl sulfoxide.<sup>37</sup> It seems reasonable to conclude that a simple anion is pyramidal especially when coordinated with an alkali metal cation. However, it is also clear that the low inversion barrier implies that a free carbanion should be effectively planar even for reactions whose rates approach the diffusion limit.

In order to compare our results for the 7-phenylnorbornyl anion with those for a simple carbanion, we required two corrections. The presence of the phenyl substituent (a practical necessity) will lower the inversion barrier, and the reduced C1-C7-C4 bond angle of the norbornyl skeleton<sup>38</sup> will raise it. It is our belief that the isoelectronic amines provide the best available model for the inversion process.<sup>39</sup> The lowering of the inversion barrier by phenyl conjugation<sup>40,41</sup> ranges from 12 kcal/mol obtained for phenyl substitution on aziridine<sup>42,43</sup> to 5 kcal/mol from comparison of aniline<sup>44</sup> and ammonia.<sup>45</sup> The inversion barrier in methyl-7-azanorbornene<sup>46</sup> is 5 kcal/mol higher than the barrier in meth-

yl-2-azaadamantane.<sup>47</sup> It thus appears that the effects of phenyl conjugation and angle strain are of comparable magnitude and opposite sign with conjugation dominant. As the 7-phenylnorbornyl anion has been found to be a planar species in solution, this observation supports the theoretical conclusion that the inversion barrier in a simple carbanion (e.g., methyl anion) should be less than 5 kcal/mol.

Our conclusions are not unique. Köbrich has reported that an acetylene-conjugated cyclopropyllithium was planar on the NMR time scale.<sup>2</sup> The inversion barrier was critically dependent on the solvent, being lower in solvents of high coordinating power. However, the possibility of contributions from bimolecular processes, which are known to influence the inversion barrier in vinylolithiums,<sup>48</sup> was not ruled out. An examination of the <sup>13</sup>C chemical shifts, especially of the para carbon, reported for benzylolithium (104.3 ppm) and benzylpotassium<sup>22c</sup> (95.2 ppm) suggest that the cation dependent structural changes reported here may also occur in simple benzyl ions. It is interesting to speculate that, in ethereal solvents, benzylolithium is pyramidal and benzylpotassium is planar. A similar influence of counterion on anion structure has been reported by Thompson and Ford.<sup>49</sup> They report that the barrier to rotation in allyllithium is substantially lower than the barrier in allylpotassium and -cesium. Lithium-induced pyramidalization is an attractive explanation. A recent review<sup>50</sup> has documented a large number of examples where the choice of alkali metal cation contributes significantly to the observed chemistry.

The results reported here support the recent theoretical conclusions that the inversion barrier in simple anions is small and less than for the isoelectronic amine. It follows that estimates of anion inversion rates, obtained by comparison of base-catalyzed hydrogen exchange with racemization rates, require reinterpretation and additional consideration given to cation and solvent effects.

**Note Added in Proof.** Recent work by Hoz and Aurbach<sup>51</sup> provides additional support for this conclusion.

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