and the path length of the cell was varied to give the proper OD for each of the three bands measured. A 1-cm cell was used for the band at about 260 nm, a 0.020-cm cell for the bands at about 210 nm, and a nominal 0.005-cm cell for the bands at about 190 nm. These were standard cylindrical cells, commercially available from Helma, and the path lengths for the shorter cells were calibrated by using an infrared spectrometer.[35] In the figures the error bars on the CD spectra indicate the repeatability for two successive scans which was exact for the B_{2u} band of (*S*)-**1**·HCl (Figure 3).

(*S*)-α-Phenylethylamine hydrochloride [(*S*)-**1**·HCl] was prepared from (*S*)-**1**, $[\alpha]^{26}_D$ −27° (*c* 2.00, CH_3OH) [lit.[10] $[\alpha]^{20}_D$ −28° (*c* 2, CH_3OH); 98.7% ee], by treatment of the latter in methylene chloride with concentrated hydrochloric acid. Recrystallization from ethanolethyl acetate gave (*S*)-**1**·HCl: mp 169–171 °C; $[\alpha]^{22}_D$ −21° (*c* 1.15, 0.1 M KOH in 4:1 CH_3OH-H_2O).

(*S*)-α-Phenylneopentylamine [(*S*)-**3**] was prepared by resolution of (±)-**3** by using *N*-acetyl-D-leucine as outlined earlier.[36] Recrystallization and decomposition of the diastereomeric salt gave (*S*)-**3**: bp 115–117 °C (28 mmHg); $[\alpha]^{25}_D$ −5.4° (neat) [lit.[36] $[\alpha]^{21}_D$ + 5.6° (neat) for the *R* isomer].

(*S*)-α-Phenylneopentylamine hydrochloride [(*S*)-**3**·HCl] was prepared from (*S*)-**3** as outlined for the preparation of (*S*)-**1**·HCl and had $[\alpha]^{25}_D$ −5° (*c* 1.60, absolute CH_3CH_2OH) [lit.[9] $[\alpha]^{26}_D$ +5.5° (*c* 2.0, absolute CH_3CH_2OH) for the *R* isomer].

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$^{13}C_2$ Labeling: A Means To Measure $^{12}C-^{13}C$ Isotopic Equilibria in 2-Norbornyl Cation

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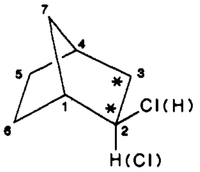
Abstract: [2,3-^{13}C]Norborn-2-yl chloride was prepared and ionized (with SbF_5) to the 2-norbornyl cation. In solution at −65 °C, rapid rearrangements occur which completely scramble the ^{13}C labels. The proton-decoupled ^{13}C NMR spectrum (62.7 MHz) contains three signals: C-4, C-1,2,6 (averaged), and C-3,5,7 (averaged). The ^{13}C labels are thus equilibrated over nonequivalent sites within the 2-norbornyl cation. This $^{12}C-^{13}C$ equilibrium isotope effect alters the proportion of di-^{13}C-labeled isomers from statistical values. The nonstatistical isotopic isomer population is manifested as an asymmetric multiplet for the averaged C-3,5,7 peak in the ^{13}C NMR spectrum. The relatively sharp lines of the multiplet can be reproduced within ±0.1 ppm, with isotopic equilibrium constants of $K_{3,5,7} = 1.010 \pm 0.005$ and $K_{1,2,6} = 1.039 \pm 0.005$.



The incorporation of ^{13}C at specific sites in organic molecules, in conjunction with ^{13}C nuclear magnetic resonance spectroscopy, can be used to obtain information about reaction mechanisms. Since the natural abundance of ^{13}C is only 1.1%, the introduced label dominates the ^{13}C NMR spectrum and label location is readily detected. ^{13}C enrichment can also aid in the study of $^{13}C-^{12}C$ kinetic[1] and/or equilibrium[2] isotope effects. Changes are also detected in ^{13}C NMR chemical shifts of nuclei[3] when they are adjacent to ^{13}C. These effects (called intrinsic shifts) are usually small, but they are experimentally measurable and useful. Most of the previous attention on ^{13}C isotope effects has been related to the kinetic isotope effects; but some results have been published on $^{13}C-^{12}C$ equilibrium isotope effects.

$^{13}C-^{13}C$ coupling constants are also of interest, since they are related to hybridization and geometry within the molecule.[4] Although methods (NMR pulse sequences exist for the observation evaluation of $^{13}C-^{13}C$ coupling in unenriched materials,[5] this approach is not without its difficulties and limitations. The introduction of ^{13}C into an organic molecule allows for determination of $^{13}C-^{13}C$ coupling constants in the molecule, with routine ^{13}C NMR spectral acquisition.[6] The couplings can be measured by

Table I. ^{13}C Chemical Shifts for the [$^{13}C_2$]Norborn-2-yl Cation[a]

carbon atom	δ at −155 °C[a,b]
1,2	124.81
3,7	36.58
4	37.86[c]
5	20.24
6	21.32

[a] In ppm, relative to Me_4Si. [b] 125.76 MHz. [c] Assigned spectral reference.

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Table II. ^{13}C Chemical Shifts for the [$^{13}C_2$]Norborn-2-yl Cation[a–c]

carbon atom	δ exptl[d]	δ calcd
1,2,6	92.08	
3,5,7 B	31.11	31.117
3,5,7 C	31.04	31.030
3,5,7 D	31.09[e]	31.100
3,5,7 E	31.25[e]	31.240
3,5,7 ref		31.135
4	37.92[f]	

[a] In ppm, relative to Me_4Si. [b] At –65 °C. [c] 62.8 MHz. [d] ±0.01 ppm. [e] Center of doublet. [f] Assigned spectral reference.

close examination of the natural abundance ^{13}C signals at the carbon center adjacent to the labeled position.

Introduction of two ^{13}C labels at adjacent sites allows for very ready measurement of the ^{13}C–^{13}C coupling constant. In many instances the introduction of two labels is no more difficult (and for norbornyl derivatives is easier) than isotopic enrichment at a single position. In cases where reaction processes promote scrambling of carbon atoms, additional ^{13}C–^{13}C coupling constants can be readily measured without additional synthesis of other dilabeled isomers.

^{13}C enrichment (at one or two position(s)) has been used in the study of carbocations and their related rearrangement processes. ^{13}C–^{13}C coupling constants have been measured, and insight has been gained about the structure of 1,4-bishomotropylium ions.[7] ^{13}C enrichment has also been used to investigate ^{12}C–^{13}C equilibrium isotope effects (and their effect on cmr chemical shift positions) for 2,3-dimethyl-2-[2-^{13}C]butylium cation[8] and 2,3-dimethylcyclopentyl cation.[9] The investigative method of ^{13}C labeling has now been applied to the 2-norbornyl cation.

Evidence that the 2-norbornyl cation has the nonclassical, bridged structure is now overwhelming. Perhaps the two most convincing results are the extremely low temperature CPMAS solid state ^{13}C NMR spectrum[10] consistent with a symmetrical cation and the deuterium isotopic perturbation study.[11] Experiments designed to obtain new data concerning this cation, in particular special properties of the interesting pentacoordinated bridging carbon, are of special interest. The incorporation of two ^{13}C atoms into a 2-norbornyl cation precursor provides the basis for such an experiment.

Discussion and Results

The known rearrangement processes in the 2-norbornyl cation (Wagner–Meerwein shift, 6,2-hydride shift, and 3,2-hydride shift) result in complete carbon scrambling.[12] The fastest scrambling processes are found to be rapid on the NMR time scale at –65 °C, where the ^{13}C NMR spectrum displays only three signals (corresponding to $C^{1,2,6}$, $C_{3,5,7}$, and C_4), compared to the five-signal spectrum at –155 °C (Table I). Exchange is thus rapid among C_3, C_5, and C_7 as well as among C_1, C_2, and C_6, at –65 °C. Close examination of the cmr spectrum of the di-^{13}C-labeled cation, at this temperature allows for experimental measurement of ^{13}C–^{12}C equilibrium isotope effects, at these two sites, within the molecule.

2,3-$^{13}C_2$]Norborn-2-yl chloride was readily synthesized from barium carbonate as the source of ^{13}C via a Diels–Alder reaction. [2,3-$^{13}C_2$]norborn-2-yl cation was prepared by ionization of the chloride with SbF_5 in SO_2ClF/SO_2F_2, at low temperature. The sample was placed in a precooled NMR probe, and spectra were recorded from –155 to –40 °C, at 125.7 and 62.8 MHz (Tables I and II).

Although at –155 °C the 6,2-hydride shift is clearly slow on the NMR time scale and spectra obtained had signals significantly narrower than those previously reported[11a] ($C_{1,2}$ width at half height of 50.3 Hz, about 0.4 ppm, as compared to 2.3 ppm at 67.8 MHz), the $C_{1,2}$, C_6, $C_{3,7}$, and C_5 peaks are still too broad to observe resolved ^{13}C–^{13}C coupling. (The ^{13}C NMR signal for C_4 is not observed since the 3,2-hydride shift necessary to migrate the ^{13}C label to this position has been suppressed by maintaining a low sample temperature.) Thus an upper limit of about 50 Hz can be placed on all coupling constants in the 2-norbornyl cation. At lower temperature, the sample froze.

Warming the sample of 2-norbornyl cation results in complete carbon scrambling. In the temperature region where the 6,2-hydride shift is fast and the 3,2-hydride shift is slow on the NMR time scale, sharp peaks are obtained and averaged ^{13}C–^{13}C coupling can be observed. At –65 °C, the averaged coupling constant between C_4 and $C_{3,5,7}$ was measured as 29.3 ± 0.2 Hz, while that between $C_{1,2,6}$ and *adjacent* ^{13}C at $C_{3,5,7}$ was found to be 33.0 ± 0.2 Hz. Coupling between nonadjacent carbons was not seen and must be smaller than the observed peak widths: 1.3 Hz for C_4, 1.9 Hz for peak B of $C_{3,5,7}$, and 3.5 Hz for peak C of $C_{3,5,7}$. [This is in sharp contrast to the relatively large C_1–C_4 coupling (over 5 Hz) which is seen in the neutral 2-norbornyl chloride (cation precursor)[13].]

On recooling the completely carbon scrambled cation to –155 °C, the signal corresponding to C_4 is now visible and appears as a triplet, with ^{13}C–^{13}C coupling of 29.4 ± 0.2 Hz. Since only one coupling is observed at this low temperature and the magnitude is equivalent to the average at higher temperature, the C_4–C_5 and C_4–$C_{3,7}$ coupling constants must be essentially identical. The averaged coupling constant between adjacent $C_{3,5,7}$ and $C_{1,2,6}$ atoms is larger than that for C_4–$C_{3,5,7}$. Clearly, one (or both) of the coupling constants C_1–C_7, C_2–C_3, and C_5–C_6 must be larger than the C_4–C_5/$C_{3,7}$–C_4 average. Since we only measure an average value, we cannot experimentally determine the relative sizes of the coupling constants.

In addition to the averaged coupling constants at –65 °C, the ^{13}C NMR spectrum also provides information on equilibria involving interchange of ^{12}C and ^{13}C between $C_{3,7}$–C_5 and between $C_{1,2}$–C_6. This information is contained in the observed ^{13}C NMR multiplets. Close examination of the ^{13}C NMR spectrum identifies the C_4 signal to be a three-line multiplet and the signal for $C_{3,5,7}$ is a six-line multiplet ($C_{1,2,6}$ is still a broad single peak). The signal for C_4 consists of a doublet (D) for the molecules where the second labeled carbon is at 3, 5, or 7 (averaged) and a central peak (A) for molecules where the other label is at carbon atoms 1, 2, or 6. As expected, peak A is exactly in the center of the doublet (D) since there is no equilibrium isotopic effect involving C_4.

The averaged signal for C_3,C_5,C_7 is more complex. The doublet D is assigned to molecules where the second label is on carbon 4. This may be done with certainty since the C_4–$C_{3,5,7}$ coupling constant is known from the C_4 signal. The singlet B is assigned to molecules where *both* labels are on carbons 3, 5, or 7. This is the most intense signal and nearly in the center of the doublet D. The doublet E is assigned to molecules where the other label is on carbons 1, 2, or 6 *adjacent* to the 3, 5, 7 carbon label. This is the only arrangement (other than C_4–$C_{3,5,7}$) that can give rise to a doublet. Peak C is assigned to molecules where the second label is on carbons 1, 2, or 6 *nonadjacent* to the 3, 5, 7 carbon label. The width of C might be due to not quite resolved 1–3 coupling. These four signals (B, C, D, E) represent all four distinguishable $^{13}C_2$-labeling situations. The relative displacements (or asymmetry) clearly result from ^{12}C–^{13}C equilibrium isotope effects.

The first isotope effect to consider is for the distribution of ^{12}C and ^{13}C among $C_{3,5,7}$ (K_1). This equilibrium constant can be obtained from the chemical shift positions of peaks that do not

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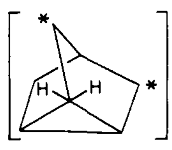
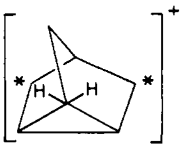
involve $C_{1,2,6}$, namely B and D. The following equations are obtained for their average frequencies:

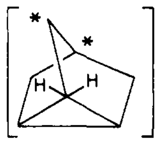


$2(\Delta/2)$

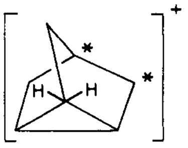


K_1

$$\delta_B = \frac{\Delta}{K_1 + 2} \tag{1}$$



$1(\Delta)$

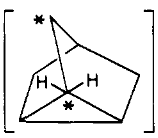


$2K_1$

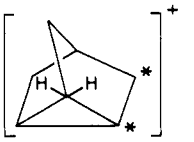
$$\delta_D = \frac{\Delta}{2K_1 + 1} \tag{2}$$

The chemical shift scale is chosen so that C_3 and C_7 are at the origin. Δ is the relative chemical shift for C_5 at −155 °C. K_1 is the equilibrium constant for exchange of ^{12}C and ^{13}C between C_5 and either C_3 or C_7. The shifts δ and δ_D would be at $\Delta/3$ in the absence of an isotope effect. A large value for K_1 favors ^{13}C at C_3 or C_7.

The second equilibrium isotope effect (K_2) involves the exchange of ^{12}C and ^{13}C between C_6 and either C_1 or C_2. This can be obtained from the positions of peaks C and E. The following equations are obtained where a large value for K_2 favors ^{13}C at C_1 or C_2.

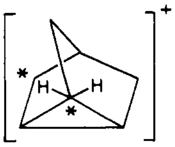


$1(\Delta)$

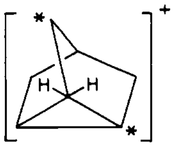


$2K_1K_2$

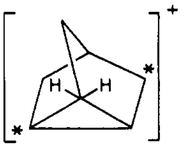
$$\delta_E = \frac{\Delta}{2K_1K_2 + 1} \tag{3}$$



K_1



$K_2(\Delta)$



K_1K_2

$$\delta_C = \frac{K_2\Delta}{K_1 + K_2 + K_1K_2} \tag{4}$$

These equations were evaluated by a computer program with use of a value of 16.34 ppm for Δ and adjusting the values for K_1, K_2, and the reference point (the unperturbed averaged $C_{3,5,7}$ peak). For values of $K_1 = 1.010$, $K_2 = 1.039$, and reference = 31.135 ppm, chemical shifts were calculated which match the experimental values within ±0.01 ppm (Table II). Although the calculated value for the reference precisely equals that derived from the ^{13}C NMR spectrum recorded at −155 °C, it was treated as a parameter in the event that changes in temperature could affect chemical shifts. (Alternatively, the value of the reference could be determined from a mixture of labeled and unlabeled 2-norbornyl cation.) Variation of either equilibrium constant by 0.005 no longer reproduced the chemical shifts within ±0.01 ppm, and this is therefore taken as the associated uncertainty.

These equilibrium constants K_1 and K_2 (measured at −65 °C), indicate an energy difference for exchange of ^{12}C and ^{13}C of 4.1 cal/mol between positions $C_{3,7}$–C_5 and a difference of 15.8 cal/mol between positions $C_{1,2}$–C_6. Since peaks B and D are shifted toward the frequency of C_5 from the isotopically unperturbed reference, there is a slight preference for ^{13}C to occupy the C_5 methylene position rather than the $C_{3,7}$ methylene position. The discrimination between $C_{1,2}$ and C_6 is larger. With doublet E shifted, relative to the isotopically unperturbed reference, toward the signal for $C_{3,7}$ (in ^{13}C NMR spectrum at −155 °C), and peak C shifted toward the signal for C_5, there is a significant bias for occupation of the pentacoordinated site by ^{12}C, rather than ^{13}C.

The lack of a large ^{12}C–^{13}C equilibrium isotope effect involving positions $C_{3,7}$–C_5 is understandable since both kinds of carbon have the same number of bonds, with similar bond strengths. This is not the case for the $C_{1,2}$–C_6 equilibrium; here, exchange is between a pentacoordinated site and a tetravalent site. In the 2-norbornyl cation, like the primary ^{13}C–^{12}C equilibrium isotope effect measured for 2,3-dimethyl-2-[2-^{13}C]butylium cation (1.0117 at −65 °C, with preference for ^{13}C over ^{12}C at the cationic site)[8], a preference is found for ^{13}C to reside in the position with fewer bonds. The size of the preference in the 2-norbornyl cation is, however, of unprecedented magnitude. To our knowledge, the experimentally determined value of 1.039 ± 0.005, at −65 °C, is the largest reported ^{13}C–^{12}C isotopic equilibrium constant.

Since heavier isotopes prefer to be at atomic positions involved in stiffer (stronger) bonds, one might guess that the pentacoordinated site, having one more bond, would be the preferred position for ^{13}C, over the tetravalent sites. However, it may be that the decreased stiffness of the (partial) bonds to the pentacoordinated carbon atom overcomes the change in the number of bonds. The same kind of reasoning was used to rationalize the results found in the 2,3-dimethyl-2-[2-^{13}C]butylium cation. If one wished to predict this isotope effect for the (hypothetical) equilibrating classical cations, one would predict an isotope effect of the same sign as that observed, but it would be hard to rationalize the magnitude of the observed effect (4% as compared with 1% found in the 2,3-dimethylbutyl ion).

Unfortunately, there is less than a 20 deg temperature window within which the 6,2-hydride shift is fast enough and the 3,2-hydride shift is slow enough for the $C_{3,5,7}$ signal to be observed without additional broadening from these processes, in the ^{13}C NMR spectrum at 62.8 MHz. (Resolution is not as good at 125.7 MHz, over a comparable temperature range, since the 6,2-shift is not completely averaged.) Therefore, a reliable study of isotopic perturbation as a function of temperature cannot be performed. By −65 °C, the label originally in the C_2 and C_3 positions completely scrambled to an equilibrium mixture of dilabeled isomers and therefore no information about the order of events during scrambling can be obtained, in this case. (Unlike the situation for the 3-nortricyclyl cation.[14])

Conclusions

Although line widths prevent J_{cc} measurement of non-averaged signals, the incorporation of ^{13}C atoms into the 2-norbornyl cation allows for the ready determination of averaged values of ^{13}C–^{13}C coupling constants. Measurements of this type are particularly efficient in molecules like the 2-norbornyl cation, which can undergo degenerate rearrangement processes that promote carbon (label) scrambling. Thus, the dilabeled precursor derived from a single synthesis is sufficient to provide information about all carbon positions in the molecule; a separate synthesis for each dilabeled isomer is not necessary.

The utility of $^{13}C_2$ labeling is not restricted to the measurement of ^{13}C–^{13}C coupling constants. In the equilibration between the nonequivalent sites $C_{3,7}$–C_5 and $C_{1,2}$–C_6, in the 2-norbornyl cation, there is a small energetic preference for ^{12}C to occupy the $C_{3,7}$ position (over C_5) and a relatively large preference for ^{12}C to occupy the C_6 position (over $C_{1,2}$). This provides information on the pentacoordinated carbon site and is consistent with the idea that the overall strength of the five (partial) bonds at the bridged carbon atom is less than that of the four bonds at the tetravalent site.

Experimental Section

[2,3-$^{13}C_2$]Norborn-2-yl Chloride. $Ba^{13}CO_3$ (20 g, 98% enriched) and magnesium powder (49.2 g, 70–80 mesh) are intimately mixed by

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[14] Saunders, M.; Jarret, R. M.; Pramanik, P. *J. Am. Chem. Soc.*, in press.

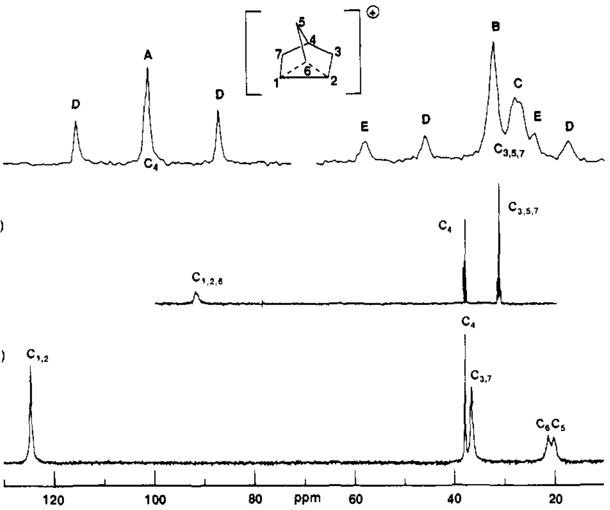

Figure 1. ${}^{13}C$-labeled norborn-2-yl cation: (a) sample in SO_2ClF at −155 °C and 125.7 MHz; (b) same sample at −65 °C and 62.8 MHz; (c) expansion of spectrum b.

grinding with a mortar and pestle and loaded into a quartz tube. The mixture is topped with a thin layer of magnesium metal. The tube is angled, stoppered, and attached to an argon supply and aspirator via a two-way stopcock. After 20 purge/evacuations, the tube is heated strongly with a Meker burner until the solid mixture ignites and the quartz tube becomes incandescent. Once cooled, the tube is attached to the base of a long condenser with a dropping funnel, filled with water, attached to the top. The condenser top also leads to a large Drierite tower, ice trap, bead filled collection U-tube in liquid nitrogen, and an oil bubbler, connected in series. A constant trickle of helium is applied (from the dropping funnel top) as the water is allowed to drip onto the barium carbide. After all the water (200 mL) is added, the solution is boiled with a heat gun for 20 min. The trap containing the fluffy white [${}^{13}C_2$]acetylene is closed off and evacuated at liquid nitrogen temperatures. The pressure change in the vacuum line (with known volume) upon warming to room temperature is used to establish the quantity of acetylene generated (35 mmol, 70%).[15] (${}^{13}C$ NMR (acetone-d_6) δ 73.4 ppm, ${}_1J^{H-{}^{13}C}$ = 297.8 Hz, ${}_2J^{H-{}^{13}C}$ = 93.0 Hz).

[${}^{13}C_2$]Acetylene (35 mmol) is transferred on the vacuum line to a 1000-mL round-botton flask containing MgO (0.3 g dissolved in 4 mL of acetic acid and 1 mL of acetic anhydride) and 5 mL of a phosphorus pentoxide/phosphoric acid/acetic acid solution (0.84 g/0.85 mL/20 mL) which has been frozen and evacuated. The reaction vessel is shaken for 20 h. The material is removed, combined with potassium acetate (1 g), and distilled to yield [1,2-${}^{13}C_2$]vinyl acetate (1.1 g, 80%), boiling point 72–74 °C (${}^{13}C$ NMR ($CDCl_3$) δ 142.0 ppm, ${}_1J^{H-{}^{13}C}$ = 189.0 Hz, δ 96.7 ppm, ${}_1J^{H-{}^{13}C}$ = 161.5 Hz, ${}_2J^{H-{}^{13}C}$ = 150.0 Hz, $J^{{}^{13}C-{}^{13}C}$ = 82.8 Hz).

[1,2-${}^{13}C_2$]Vinyl acetate (4 g) and cyclopentadiene (4.5 mL) are placed in a sealed tube and heated to 200 °C for 14 h. The contents are distilled and in addition to recovering about half of the starting acetate, [2,3-${}^{13}C_2$]norbornen-5-yl acetate (1.8 g) is obtained, boiling point 82–83 °C at 17 Torr (${}^{13}C$ NMR ($CDCl_3$) δ 74.8 ppm, ${}_1J^{H-{}^{13}C}$ = 158.5 Hz, δ 34.8 ppm, ${}_1J^{H-{}^{13}C}$ = 134.5 Hz, $J^{{}^{13}C-{}^{13}C}$ = 44.1 Hz).

[2,3-${}^{13}C_2$]Norbornen-5-yl acetate is essentially quantitatively converted to [2,3-${}^{13}C_2$]norborn-2-yl acetate by stirring overnight in ethyl acetate with PtO_2, under an atmosphere of H_2. The reaction was carried out on a vacuum line where upon completion the material could be transferred and collected, free from solvent and catalyst (${}^{13}C$ NMR (in ethyl acetate) endo: δ 75.5 ppm, ${}_1J^{H-{}^{13}C}$ = 150.8 Hz, δ 37.2 ppm, ${}_1J^{H-{}^{13}C}$ = 134.7, $J^{{}^{13}C-{}^{13}C}$ = 36.5 Hz; exo: δ 77.3 ppm, ${}_1J^{H-{}^{13}C}$ = 156.3 Hz, δ 39.8 ppm, ${}_1J^{H-{}^{13}C}$ = 130.8, $J^{{}^{13}C-{}^{13}C}$ = 34.4 Hz).

[2,3-${}^{13}C_2$]Norborn-2-yl acetate (0.5 g) is added to anhydrous methanol (30 mL), containing catalytic amounts of sodium metal (introduced slowly). The reaction mixture is heated to reflux, overnight. Methanol is removed by distillation through a beaded column, and the remains are taken up in ether and acid washed. The ether is then also removed by distillation through a beaded column, leaving (0.4 g) [2,3-${}^{13}C_2$]norborn-2-yl alcohol (${}^{13}C$ NMR (CCl_4) endo: δ 71.9 ppm, ${}_1J^{H-{}^{13}C}$ = 146.5 Hz, δ 38.9 ppm, ${}_1J^{H-{}^{13}C}$ = 131.6 Hz; exo: δ 73.8 ppm, δ 41.6 ppm, ${}_1J^{H-{}^{13}C}$ = 127.7 Hz, $J^{{}^{13}C-{}^{13}C}$ = 34.1 Hz).

[2,3-${}^{13}C_2$]Norborn-2-yl alcohol (0.4 g) is placed in a flask along with triphenylphosphine (2.2 g) and CCl_4 (35 mL) and refluxed for 16 h. Pentane is added to the cooled solution until precipitate formation ceased. The precipitate is filtered off and the solvent is removed by distillation through a beaded column, yielding (0.3 g) [2,3-${}^{13}C_2$]norborn-2-yl chloride (${}^{13}C$ NMR (Me_2SO-d_6) endo: δ 61.2 ppm, δ 40.3 ppm, $J^{{}^{13}C-{}^{13}C}$ = 34.6; exo: δ 62.4 ppm, ${}_1J^{H-{}^{13}C}$ = 164.6 Hz, δ 42.9 ppm, ${}_1J^{H-{}^{13}C}$ = 135.9 Hz, $J^{{}^{13}C-{}^{13}C}$ = 32.0 Hz). The sample is further purified by preparative gas chromatography with a 4-ft UV-101 column, at an oven temperature of 120 °C.

Cation Sample Preparation. [2,3-${}^{13}C_2$]norborn-2-yl cation is prepared in the molecular beam apparatus[15] by codistillation of the corresponding chloride (0.015 g) and SbF_5 (in a 1 to 4 molar ratio) under vacuum, with subsequent addition of SO_2CF/SO_2F_2 (2.0 mL of a 50:50 mixture by volume at −78 °C; other solvent ratios were investigated but equal amounts gave the best results). The mixture is warmed from liquid nitrogen temperatures to −110 °C and, while still under vacuum, poured into an NMR tube at the lowest possible working temperature so as to suppress extensive 3–2 hydride shifts, which would scramble the ${}^{13}C$ labels. The sample is placed in a precooled NMR probe and spectra recorded from −155 to −40 °C, at 125.7 and 62.8 MHz (Tables I and II).

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Registry No. $BaCO_3$, 513-77-9; ${}^{13}C$, 14762-74-4; 2-norbornyl cation, 24321-81-1; [${}^{13}C_2$]-2-norbornyl cation, 107658-45-7; *endo*-[2,3-${}^{13}C_2$]-norborn-2-yl chloride, 106139-44-0; barium carbide, 12070-27-8; [${}^{13}C_2$]-acetylene, 35121-31-4; [1,2-${}^{13}C_2$]-vinyl acetate, 106139-40-6; [2,3-${}^{13}C_2$]-norborn-5-en-2-yl acetate, 107658-46-8; *endo*-[2,3-${}^{13}C_2$]-norborn-2-yl acetate, 106139-42-8; *exo*-[2,3-${}^{13}C_2$]-norborn-2-yl acetate, 106139-46-2; *endo*-[2,3-${}^{13}C_2$]-norborn-2-yl alcohol, 106139-43-9; *exo*-[2,3-${}^{13}C_2$]-norborn-2-yl alcohol, 106139-47-3; *exo*-[2,3-${}^{13}C_2$]-norborn-2-yl chloride, 106139-48-4; cyclopentadiene, 542-97-7.

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