H. A. Craig made much of this work possible.

Registry No. 4a, 88686-46-8; **4a**·HBr, 105858-01-3; **4b**, 105858-04-6; **4b**·HBr, 105858-03-5; **4c**, 105858-06-8; **4c**·HBr, 105858-05-7; **8**, 96412-32-7; **9**, 105881-93-4; **10**, 105858-17-1; **11**, 105881-94-5; DitBuADPO, 88686-45-7; DitBuADAsO, 93684-26-5; DitBuADSbO, 105858-07-9; DiAdADPO, 105858-08-0; DiAdADAsO, 105858-09-1; DiAdADSbO, 105858-10-4; DiPhADAsO, 105858-11-5; DiPhADSbO, 105858-12-6; DitBuADPO·HOTf, 105858-14-7; DitBuADAsO·HOTf, 105858-16-0; DitBuADPO·*o*-Chloranil, 105858-18-2; DitBuADAsO·*o*-Chloranil, 105858-29-5; DitBuADSbO·*o*-Chloranil, 105858-30-8; DitBuADPO·HFBA, 105881-95-6; DitBuADPO·HFB, 105858-19-3; DitBuADPO·2HFB, 105858-20-6; DitBuADAsO·HFBA, 105858-31-9; DitBuADAsO·2HFB, 105899-58-9; DitBuADSbO·HFBA, 97921-06-7; DitBuADSbO·2HFBA, 105858-33-1; DitBuADSbO·2HFB, 105858-21-7; DitBuADPO·Cl_2, 105858-22-8; DitBuADPO·Br_2, 105858-23-9; DitBuADSbO·Cl_2, 105858-24-0; DitBuADPO·CH_3/Cl, 105858-26-2; DitBuADPO·$(CH_3)_2$, 105858-27-3; DitBuADAsO·Cl_2, 105858-25-1; DitBuADPO·HF_3, 105858-34-2; HFBA, 685-24-5; HFB, 692-50-2; TASF, 105858-28-4; $[(DitBuADSbO)Pt(PPh_3)_2(CH_3)]^+SbF_6^-$, 104130-28-1; $(DitBuADPO)_2PtI_2$, 99688-40-1; $(DitBuADSbO)_2PtI_2$, 104130-26-9; $[((CH_3)_2C{=}O)(PPh_3)_2PtCH_3]^+SbF_6^-$, 104130-30-5; 1-bromo-3,3-dimethyl-2-butanone, 5469-26-1; 5-aza-5-benzyl-2,2,8,8-tetramethyl-3,7-dione hydrobromide, 105858-00-2; benzylamine, 100-46-9; 1-adamantylbromomethyl ketone, 5122-82-7; 3-aza-3-benzyl-1,5-di-1-adamantylpentane-1,5-dione hydrobromide, 105858-02-4; α-bromoacetophenone, 70-11-1; 3-aza-3-benzyl-1,5-diphenylpentane-1,5-dione hydrobromide, 31410-17-0; *o*-chloranil, 2435-53-2; triphenylphosphine, 603-35-0; triphenylarsine, 603-32-7; triphenylantimony, 603-36-1; triphenylphosphine tetrachlorocatecholate, 62475-98-3; triphenylarsine tetrachlorocatecholate, 86780-28-1; triphenylantimony tetrachlorocatecholate, 86780-29-2; (1,5-cyclooctadiene)platinum(II) iodide, 12266-72-7.

Supplementary Material Available: A complete description of the X-ray crystallographic structure determinations, including experimental procedures, tables of data, and stereodrawings (297 pages). Ordering information is given on any current masthead page.

Carbon Scrambling and ^{13}C–^{13}C Coupling Constants in ^{13}C NMR Spectra of 2-Norbornyl Chloride

Ronald M. Jarret and Martin Saunders*

Contribution from the Sterling Chemistry Laboratory, Yale University, New Haven, Connecticut 06511. *Received June 16, 1986*

Abstract: 2-Norbornyl-*2,3*-$^{13}C_2$ chloride undergoes carbon scrambling in nitrobenzene induced by a catalytic amount of $SnCl_4$, evidently by reversible ionization. ^{13}C NMR spectra show approach to equilibrium, in days, at 5 °C. The order of isomer appearance is completely explained through the Wagner–Meerwein, 6–2 hydride, and 3–2 hydride shifts. A possible rearrangement via the norpinyl cation was shown to be at least 20 times slower than the 3–2 hydride shift at room temperature. ^{13}C–^{13}C coupling was measured, using standard ^{13}C NMR, for all pairs of carbon atoms in the scrambled 2-norbornyl chloride. A single di-^{13}C-labeled precursor thus generated all of the dilabeled isomers in a controlled fashion, yielding both mechanistic information concerning the rearrangement and all the ^{13}C–^{13}C coupling constants.

^{13}C–^{13}C coupling constants are of interest for several reasons. They may be empirically correlated with bonding in the case of adjacent atoms or with molecular geometry in the case of nonadjacent atoms or compared with theoretically calculated values. Although, NMR pulse sequences exist for obtaining ^{13}C–^{13}C coupling constants from compounds without enrichment above natural abundance,[1] the signal-to-noise ratio is usually extremely poor and/or the time of acquisition extremely long. ^{13}C–^{13}C coupling constants have also been obtained from monolabeled substances,[2] but one still must observe the unenriched signal in the ^{13}C NMR and the ^{13}C still needs to be synthetically introduced. In many cases it is no more difficult to incorporate a second ^{13}C. In fact, for the norbornyl system, it is easier to make the dilabeled material. As a result of the scrambling processes which occur readily in the norbornyl system, it is possible to observe all of the di-^{13}C-labeled isomers and thus measure all of the coupling constants starting with a single initial isomer, directly observing signals from the enriched carbons in the ^{13}C NMR. J_{12} for both *endo*- and *exo*-2-norbornyl-*2,3*-$^{13}C_2$ acetate and 2-norbornyl-*2,3*-$^{13}C_2$ alcohol were obtained in the course of the synthesis of 2-norbornyl-*2,3*-$^{13}C_2$ chloride.

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(2) (a) Marshall, J. L.; Miiller, D. E. *J. Am. Chem. Soc.* **1973**, *95*, 8305. (b) Barfield, M.; Burfitt, I.; Doddrell, D. *J. Am. Chem. Soc.* **1975**, *97*, 2631 and references cited within.

Table I. ^{13}C NMR Chemical Shifts in 2-Norbornyl Chloride[a]

carbon	exo δ,[b] ppm	endo δ,[b] ppm
1	46.7	44.3
2	63.1	62.0
3	43.9	41.3
4	37.2	37.8
5	28.5	30.0
6	27.0	22.7
7	35.4	38.3

[a] ^{13}C NMR at 62.8 MHz, with 0.116 Hz/pt, at 35 °C. [b] In nitrobenzene-d_5 (downfield most peak set to 149.5 ppm, from Me_4Si).

Results and Discussion

To obtain mechanistic information on rearrangements which scramble carbon atoms and to measure a complete array of ^{13}C–^{13}C coupling constants in a 2-norbornyl system, the following experiment was performed. 2-Norbornyl-*2,3*-$^{13}C_2$ chloride was placed in dimethyl-d_6 sulfoxide (Figure 1a) and heated. At 150 °C, coupled signals corresponding to C_1 and C_7 simultaneously appeared (assignments taken from literature,[3] Table I), indicating effective Wagner–Meerwein rearrangement, presumeably via ionization to the nonclassical cation and return of chloride. Elimination had also begun to take place, creating di-^{13}C-labeled nortricyclane (^{13}C–^{13}C coupling = 43.0 Hz for cyclopropane

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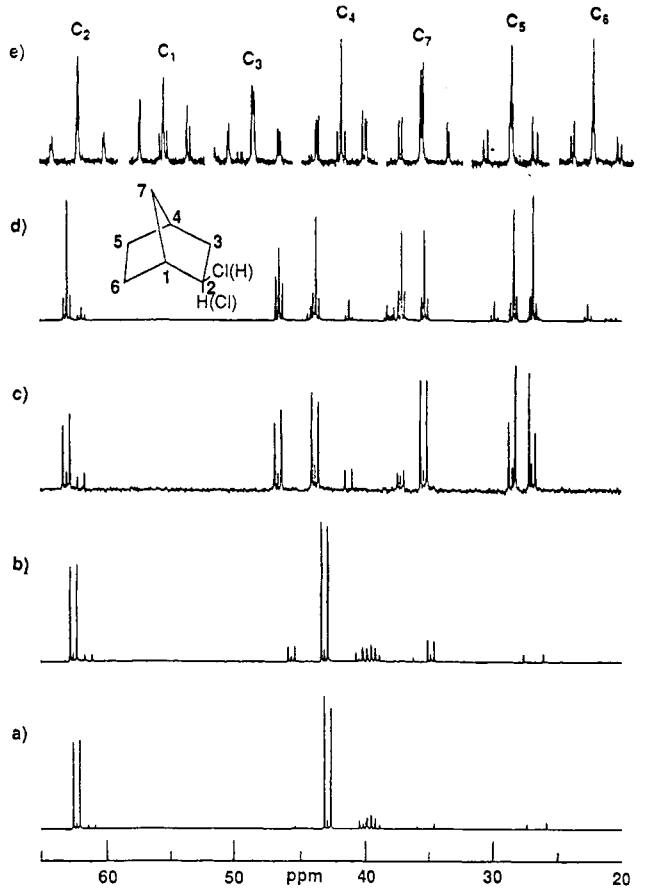
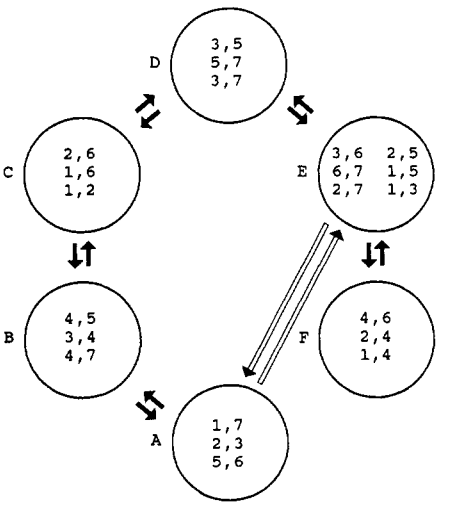


Figure 1. 2-Norbornyl-$^{13}C_2$ chloride at 62.8 MHz: (a) Me_2SO-d_6, room temperature for 1 h; (b) Me_2SO-d_6/HCl, 125 °C for 2 h; (c) nitrobenzene-d_5/$SnCl_4$, room temperature for 1 h; (d) nitrobenzene-d_5/$SnCl_4$, room temperature for 7 days; and (e) expansion of spectrum d.

CH_2).[4] No other products (norbornene, etc.) were observed. Gaseous HCl was introduced to attempt reversal of the elimination and catalysis of further scrambling rearrangements (Figure 1b). Although the acid did seem to suppress elimination and promote cation formation, at elevated temperatures (150 °C) the Me_2SO decomposed. The 2-norbornyl-2,3-$^{13}C_2$ chloride was recovered from this mixture by preparative gas chromatography (4 ft OV-101 column at 120 °C) and dissolved in nitrobenzene-d_5 with a catalytic amount of $SnCl_4$ (3–5%). The first NMR taken after the mixture had been prepared (Figure 1c) showed that extensive scrambling had occurred. That is, coupled signals for C_1, C_2, C_3, C_5, C_6, C_7 were of comparable intensities and C_4 was also observed (5–6% of total ^{13}C NMR integration). There was also a detectable increase in the center peak (uncoupled, not adjacent to the other label) for C_2 and C_6, relative to the other carbon signals. This is as expected, considering the mechanistic pathway in Scheme I.

Since norpinyl reactants commonly rearrange to norbornyl products on solvolysis,[5] another possible scrambling process which we considered was the reversible uphill rearrangement to the norpinyl cation, leading to the interchange of C_3 with C_7. This process would not have been seen in our earlier study of the 3–2 hydride shift[6] even if it had been faster than the 3–2 shift, since it does not interchange any *protons* which are not already being rapidly interchanged. Although there was no obvious indication of this norpinyl rearrangement in the ^{13}C NMR spectrum, a RUNGE-KUTTA numerical integration program[7] was used to simulate the pathways depicted in Scheme I in order to determine

Scheme I



Rearrangement Pathways for dilabeled Norbornyl Chloride. Isomers within each circle are interconverted by Wagner-Meerwein and 6-2 hydride shift processes. Solid arrows represent 3-2 hydride shifts and open arrows indicate the norpinyl rearrangement.

Table II. ^{13}C–^{13}C Coupling Constants in 2-Norbornyl-$^{13}C_2$ Chloride[a]

carbon pair	exo $J^{13C-13C}$ (+/− 0.1 Hz)	endo $J^{13C-13C}$ (+/− 0.3 Hz)
1,2	33.6	33.9
1,6	31.1	32.7
1,7	31.6	31.3
2,3	31.9	34.1
3,4	31.5	32.2
4,5	32.2	32.8
4,7	30.4	24.4[c]
5,6	31.7	31.1
1,3	1.3	
1,4	5.1	5.1
5,7	1.7	
6,7	1.7	

[a] ^{13}C NMR at 62.8 MHz, with 0.116 Hz/pt, in nitrobenzene-d_5, at 35 °C. [b] Carbon pairs not represente have a coupling constant less than 1 Hz. [c] A larger uncertainty must be placed here, due to complexity of region in ^{13}C NMR.

a limit for the rate of the norpinyl rearrangement (relative to the 3–2 hydride shift).

The 21 di-^{13}C-labeled isomers fall into five groups of three and one of six: the isomers of each group interconnected by Wagner–Meerwein and 6–2 hydride shifts. Since these processes are very much faster than the 3–2 hydride shift, we treated these groups as entities for simplicity. These six groups of isomers are connected with each other by 3–2 hydride shifts and (possibly) the norpinyl rearrangement pathway as indicated. A spectrum taken immediately after addition of $SnCl_4$ showed that only the isomers of groups A, B, and C were detectably populated (86%, 11%, 2%, respectively). If the norpinyl rearrangement were occurring even 1/20 as fast as the 3–2 hydride shift, the isomers of group E would be at the same detectable level as those of group C. Therefore, the norpinyl rearrangement occurs at a rate less than 1/20 as fast as the 3–2 hydride shift at room temperature.

After several days at 5 °C, an equilibrium mixture (equal quantities) of the di-^{13}C-labeled 2-norbornyl chloride isomers was achieved for the endo and exo compounds (Figure 1d). *exo*-2-norbornyl chloride is favored by a 5.0-to-1 ratio over endo in nitrobenzene-d_5. Chemical shift assignments for the endo chloride are based on measured coupling constants and analogous findings in published assignments for 2-norbornanol[8] (Table I). The signal for each carbon atom is a complex multiplet as a result of multiple couplings. Many coupled signals are not exactly symmetric about

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(5) Kirmse, W. *Acc. Chem. Res.* **1986**, *19*, 36 and references cited.
(6) Saunders, M.; Schleyer, P. v. R.; Olah, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 5680.
(7) Computer program is available from authors.
(8) Stothers, J. B.; Tan, C. T.; Teo, K. C. *Can. J. Chem.* **1976**, *54*, 1211.

the central peak; this asymmetry (less than 2 Hz) may be due to ^{12}C–^{13}C intrinsic shifts in the neutral molecule.[9]

All ^{13}C–^{13}C coupling constants in the chloride can thus be measured starting with a single initial isomer (Table II). All the measured coupling constants between pairs of bonded carbons in both *exo*- and *endo*-2-norbornyl chloride are within the normal range for sp^3 bonds.[2a] However, the C_4-C_7 coupling constant in both the endo and exo chlorides, is smaller than any other coupling constant between adjacent carbon atoms. The C_1–C_2 coupling constant is the largest in the exo compound and is clearly larger than that for C_2–C_3. In contrast, in the endo compound, the C_2–C_3 coupling constant is found to be slightly larger than that for C_1–C_2. One might imagine that this is an indication of polarization in the exo isomer in the direction of the nonclassical ion. The C_2–C_3 coupling constant in the endo might be taken as an indication of incipient elimination.

Nonadjacent ^{13}C–^{13}C couplings in the *exo*-2-norbornyl chloride are also observed and except for C_1–C_4 are of the magnitude normally associated with J_{13} couplings[2] (0–2 Hz) or J_{14} couplings[2a] with a dihedral angle near 65° (0–1 Hz). J_{14} is shown to be about 2 Hz, when a dihedral angle of 0° exists between the two ^{13}C atoms, reaching a minimum of 0 Hz with an angle of 65° and a maximum of 5–6 Hz with a dihedral angle of about 170°. Coupling between bridgehead carbons in bicyclic rings has been shown to be a sensitive function of the bridge sizes.[10]

Conclusions

All ^{13}C–^{13}C coupling constants in a molecule can be obtained starting with a single di-^{13}C-labeled isomer if rearrangements occur which completely scramble the carbons. This technique has been applied to the 2-norbornyl system, using 2-norbornyl-*2,3*-$^{13}C_2$ chloride in nitrobenzene-d_5 with $SnCl_4$ as catalyst, at room temperature. Conditions promoting cation formation of sufficient lifetime to allow carbon scrambling, followed by recapture, are required. A scrambling rearrangement might be applied at any stage in a synthetic scheme in order to obtain scrambled product yielding a complete set of ^{13}C–^{13}C coupling constants for a desired molecule.

Experimental Section

2-Norbornyl-*2,3*-$^{13}C_2$ Chloride. $Ba^{13}CO_3$ (20 g, 98% enriched) and magnesium powder (49.2 g, 70–80 mesh) were intimately mixed by grinding with mortar and pestle and loaded into a quartz tube. The mixture was topped with a thin layer of magnesium metal. The tube was angled, stoppered, and attached to an argon supply and aspirator via a two-way stopcock. After 20 purge/evacuations, the tube was heated strongly with a Meker burner until the solid mixture ignited and the quartz tube became incandescent. Once cooled, the tube was attached to the base of a long condenser with a dropping funnel, filled with water, and attached to the top. The condenser top also led 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 was applied (from the dropping funnel top) as the water was allowed to drip onto the barium carbide. After all the water (200 mL) had been added, the solution was brought to boil with a heat gun for 20 min. The trap containing the fluffy white [$^{13}C_2$]acetylene was closed off and evacuated at liquid nitrogen temperatures. The pressure change in the vacuum line (with known volume) upon warming to room temperature was used to establish the quantity of acetylene generated (35 mmol, 70%).[11] (^{13}C NMR: (acetone-d_6) δ 73.4 ($_1J^{H-^{13}C}$ = 297.8 Hz, $_2J^{H-^{13}C}$ = 93.0 Hz.)

[$^{13}C_2$]Acetylene (35 mmol) was transferred on the vacuum line to a 1000 mL round-bottom 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 had been frozen and evacuated. The reaction vessel was shaken for 20 h. The material was removed, combined with potassium acetate (1 g), and distilled to yield vinyl-*1,2*-$^{13}C_2$ acetate (1.1 g, 80%), bp 72–74 °C. (^{13}C NMR: ($CDCl_3$) δ 142.0 ($_1J^{H-^{13}C}$ = 189.0 Hz), 96.7 ($_1J^{H-^{13}C}$ = 161.5 Hz, $_2J^{H-^{13}C}$ = 150.0 Hz, $J^{^{13}C-^{13}C}$ = 82.8 Hz.)

Vinyl-*1,2*-$^{13}C_2$ acetate (4 g) and cyclopentadiene (4.5 mL) were placed in a sealed tube and heated to 200 °C for 14 h. The contents were distilled and in addition to recovering about half of the starting acetate 5-norbornenyl-*2,3*-$^{13}C_2$ acetate (1.8 g) was produced, bp 82–83 °C (17 Torr). (^{13}C NMR: ($CDCl_3$) δ 74.8 ($_1J^{H-^{13}C}$ = 158.5 Hz), 34.8 ($_1J^{H-^{13}C}$ = 134.5 Hz, $J^{^{13}C-^{13}C}$ = 44.1 Hz.)

5-Norbornenyl-*2,3*-$^{13}C_2$ acetate was essentially quantitatively converted to 2-norbornyl-*2,3*-$^{13}C_2$ 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 ($_1J^{H-^{13}C}$ = 150.8 Hz), 37.2 ($_1H^{H-^{13}C}$ = 134.7, $J^{^{13}C-^{13}C}$ = 36.5 Hz); exo, δ 77.3 ($_1J^{H-^{13}C}$ = 156.3 Hz), 39.8 ($_1J^{H-^{13}C}$ = 130.8, $J^{^{13}C-^{13}C}$ = 34.4 Hz.)

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

2-Norbornyl-*2,3*-$^{13}C_2$ alcohol (0.4 g) was placed in a flask along with triphenylphosphine (2.2 g) and CCl_4 (35 mL) and refluxed for 16 h. Pentane was added to the cooled solution until precipitate formation ceased. The precipitate was filtered off and the solvent was removed by distillation through a beaded column, yielding (0.3 g) 2-norbornyl-*2,3*-$^{13}C_2$ chloride. (^{13}C NMR: (Me_2SO-d_6) endo, δ 61.2, 40.3 ($J^{^{13}C-^{13}C}$ = 34.6); exo, δ 62.4 ($_1J^{H-^{13}C}$ = 164.6 Hz), 42.9 ($_1J^{H-^{13}C}$ = 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.

Acknowledgment. This work was supported by a grant from the National Science Foundation. R.M.J. acknowledges support by a fellowship administered by the American Chemical Society Division of Organic Chemistry and sponsored by the Proctor and Gamble Co.

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