

Nortricyclyl-Norbornenyl Cation. Isotopic Perturbation and Isotopic Scrambling

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Abstract: The stable carbocation which is formed from either 3-nortricyclyl or norbornenyl precursors was studied with the deuterium isotopic perturbation method. ^{13}C NMR signals from the two carbons, expected to be widely split by isotopic perturbation if an equilibrium exists between rapidly interconverting norbornenyl structures, showed only a small, temperature-independent splitting. It was concluded that a maximum of $\sim 1\%$ of the equilibrating norbornenyl ions might be present. A single structure (nortricyclyl with extensive charge delocalization) adequately represents the cation. This is verified by di- ^{13}C -labeled cation precursor, which also provides the complete set of $J_{12}^{13\text{C}-^{13}\text{C}}$ coupling constants. NMR spectra of the deuterated ion and of 1,7-di- ^{13}C -labeled ion revealed that the cation is undergoing at least three different scrambling processes below 0°C . The spectra show that the fastest process involves reversible skeletal rearrangement to the bicyclo[3.1.1]heptenyl cation. A still slower process including a hydride shift also occurs. The observed rearrangements ultimately result in *complete scrambling of all carbons and hydrogens in the cation.*

The nature of the intermediate carbocation(s) involved in the solvolysis of norbornenyl and nortricyclyl derivatives has long been a matter of controversy.^{1,2} Mixtures of norbornenyl and nortricyclyl products are obtained from either type of precursor. To explain the product distribution, many authors have postulated the existence of an equilibrium between the symmetric nortricyclyl and a rapidly equilibrating pair of asymmetric norbornenyl cations (Figure 1); some authors have depicted these intermediates as nonclassically bridged with delocalized charge.

In 1975, Olah and Liang² prepared a stable cation solution from a nortricyclyl precursor. On the basis of low-field resonances in the ^1H and ^{13}C NMR spectra obtained at -80°C , they concluded that the cation had the localized nortricyclyl structure. However, it is by now well-known that ^{13}C NMR chemical shifts, by themselves, are unreliable indicators of the distribution of charge in cations since they are as strongly affected by hybridization and other bonding effects. ^1H NMR shifts are influenced considerably by magnetic anisotropy. Delocalization of charge is another complicating factor. Therefore, it is not possible to accurately predict the chemical shifts of either the extreme nortricyclyl nor norbornenyl structures for the cation from known models.

While it might be concluded that the peak positions seem to fit the nortricyclyl structure more closely than a rapidly equilibrating pair of norbornenyl structures, it is impossible to rule out a rapid equilibrium between nortricyclyl and norbornenyl structures. For example, 30% of norbornenyl cations in equilibrium with 70% nortricyclyl cation could easily give the observed chemical shifts.

The method of isotopic perturbation³ is an effective means of detecting such equilibria. If any considerable fraction of the ion had the norbornenyl structure, undergoing rapid interconversion between the enantiomers, the C_1 and C_2 carbons, would give a single averaged peak in the ^{13}C NMR spectrum. However, deuterium substitution on C_3 would be expected to perturb this equilibrium and thereby substantially (and with temperature dependence) split this single resonance into two lines.

Results

Although, other workers' attempts to prepare the cation from 2-hydroxy- and 2-chloro-5-norbornene precursors failed,² we have successfully and reproducibly prepared the cation from 2-cation-5-norbornene by using a modification of the previously described "Molecular Beam" method.⁴ The cation system was

studied by using ^{13}C , ^1H , and ^2H NMR spectroscopy. As expected from the solvolysis studies, either the nortricyclyl or norbornenyl precursor produces a stable solution of the same cation(s).

The ^{13}C NMR spectrum of the C^3 -dideuterated cation prepared from a mixture of norbornenyl and nortricyclyl chlorides *does* show two peaks in the region of C_1/C_2 resonance. The splitting however is only 0.7 ppm at -110°C in contrast to the ~ 90 ppm expected for a rapidly equilibrating mixture of only norbornenyl cations (using methylene-deuterated dimethylcyclopentyl cation as a model).⁵ It is also significant that the small splitting observed remained unchanged (and did not show the large temperature dependence associated with perturbation of rapid equilibria) over the temperature range -50 to -110°C .

At temperatures above -50°C , the proton-decoupled ^{13}C NMR spectrum becomes more complex, as small new peaks appear near the original ones. We suspected that the changes in the ^{13}C NMR spectrum were due to rearrangements of the deuterium to other positions and therefore took ^2H NMR spectra. Samples prepared and observed at low temperature showed only the peaks for the exo and endo deuteriums. However, when the dideuterated cation was heated above -50°C , one of the two original deuterium signals decreased, at the same time as the signals for the *four other types of hydrogen grew in simultaneously*. Cations were also generated from both the endo and exo 3-deuterio-5-norbornen-2-yl chloride and 3-deuterionortricyclyl-5-yl chloride. (The assignment of the exo and endo proton shifts in the precursor had been established with the aid of NMR-shift reagents.) NMR of the mono-deuterated cations (at C_3) demonstrates that it is the deuterium nearest the positive charge (exo) that rearranges to the four other positions on heating above -50°C . At $\sim 0^\circ\text{C}$, the endo deuterium (furthest from the positive charge) finally also scrambles.

A number of mechanistic possibilities were considered for the scrambling. However, the observation that the migrating deuterium appeared at *all four* other positions at close to statistical probabilities in the initial stage of the scrambling was most difficult to accommodate. We finally concluded that the only way in which this could happen was intervention of one or more other processes, *more rapid* than the deuterium scrambling which we first saw.

In the search for processes occurring faster than the initial rearrangement observed, cations were generated from precursors with deuterium labels, originally present at positions other than exo and endo. The low-temperature ^2H NMR spectrum of the cation generated from 2-deuterio-5-norbornen-2-yl chloride, indicated that no scrambling had occurred during sample preparation. At temperatures above -70°C , the signal corresponding to deuterium on C_2 decreases in intensity as the signals corresponding to that on C_4 and that on C_5 simultaneously grow in;

(1) Barkhash, V. A. In *Topics in Current Chemistry*; Rees, C. W., Ed.; Springer-Verlag: Heidelberg, FRG, 1984; Vol. 116/117.

(2) Olah, G. A.; Liang, G. *J. Am. Chem. Soc.* **1975**, *97*, 1920.

(3) Saunders, M. In *Stereodynamics of Molecular Systems*; Sarma, R. M., Ed.; Pergamon: Elmsford, NY, 1979.

(4) Saunders, M.; Cox, D.; Lloyd, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 6656. Calibrated containers were used for both the organic halide and SbF_5 , so as to monitor/regulate the rate of codeposition. A molar rate ratio of about 0.025:1 (RX: SbF_5) was used.

(5) Saunders, M.; Telkowski, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070.

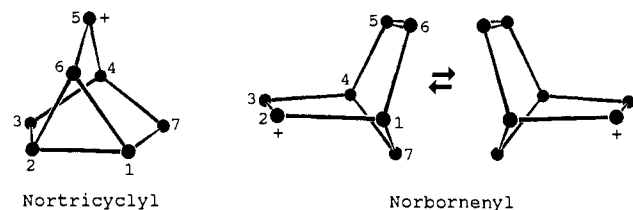


Figure 1.

hence, a more rapid process is occurring. At temperatures above $-50\text{ }^{\circ}\text{C}$, the signals corresponding to *all other* positions appear and finally approach the expected intensities corresponding to complete equilibrium.

With 5-deuterionortricycl-5-yl chloride as precursor, the cation was generated, and at temperatures above $-70\text{ }^{\circ}\text{C}$, the signal corresponding to that on C_5 (in the ^2H NMR spectrum) decreases in intensity as the signals corresponding to that on C_2 first and followed by that on C_4 grow in. At temperature above $-50\text{ }^{\circ}\text{C}$, the signals corresponding to all other positions grow in.

Convincing evidence for proton scrambling can also be obtained by using a ^1H NMR pulse sequence to detect magnetization transfer. This technique has several attractive features: 1. Proton scrambling can be detected at lower temperatures than would be required to produce measurable line broadening in the ^1H NMR spectrum. 2. No isotopic enrichment is necessary to observe rearrangement reactions. 3. The particular protons involved in the interchange are immediately identified.

At temperatures above $-35\text{ }^{\circ}\text{C}$, magnetization transfer was found to take place in the nortricycyl cation. Saturation of the protons on C_1 results in a substantial decrease in signal intensity of protons on C_4 and C_5 . Saturation of the C_4 proton causes a substantial decrease in signal intensity of protons on C_1 and C_5 . Saturation of the proton on C_5 results in a substantial decrease in signal intensity of the C_1 and C_4 protons.

In attempting to explain the deuterium scrambling and magnetization transfer results, we still had to consider two types of processes which might occur. One type results in hydrogen migration from one carbon to another (perhaps via hydride shifts) without disturbing the carbon framework. A second type would involve carbon skeletal rearrangements *without* breaking any C-H bonds. To gain more insight, particularly on the second reaction type, a cation was generated from 2,3- $^{13}\text{C}_2$ -nortricycl-5-yl chloride. The proton-decoupled ^{13}C NMR spectrum (Figure 2) initially shows two doublets (each with a tiny central peak: enriched position adjacent to ^{12}C site), corresponding to C_2 and C_3 (coupled to each other).

At $-70\text{ }^{\circ}\text{C}$, a doublet corresponding to C_4 grows in (coupled to C_3) and C_5 appears as a singlet. The tiny central peaks of the original doublets from C_2 and C_3 (corresponding to enriched uncoupled carbons) increase in intensity. In the presence of an external standard, CD_2Cl_2 in SO_2ClF , integrations of the ^{13}C NMR spectrum acquired with inverse-gated decoupling show that the area of C_3 is not diminished and that C_2 is solely responsible for the appearance of the other signals. When allowed to come to equilibrium at $-50\text{ }^{\circ}\text{C}$, signals corresponding to C_5 , C_4 , C_2 , and C_3 are present in the ratio of 1:1:2:4, respectively. This scrambling results in the sequential appearance of the ^{13}C satellites in the ^1H NMR spectrum, which verifies the spectral assignments.

At temperatures above $-50\text{ }^{\circ}\text{C}$, the final signal corresponding to C_6 appears in the ^{13}C NMR spectrum, and with prolonged heating at these temperatures, all possible permutations of the ^{13}C -dilabel are demonstrated by the splitting patterns at each ^{13}C NMR resonance. After scrambling is allowed to continue to near completion, each pair of ^{13}C - ^{13}C coupling constants can be experimentally measured (Table I) and used to verify spectral assignments and gain insight into details on structure of the cation. Quantum mechanical calculations at the 6-31g//6-31g level were also performed for the latter purpose.

Discussion

The experimental results support the existence of at least *three* degenerate rearrangement reactions occurring at or below $0\text{ }^{\circ}\text{C}$.

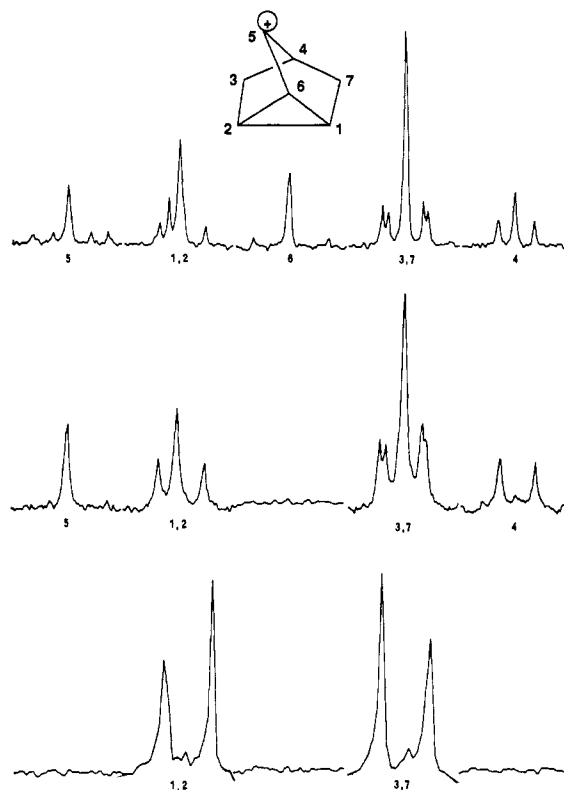


Figure 2.

Table I. Experimentally Measured ^{13}C - ^{13}C Coupling Constant

atom pair	^{13}C - ^{13}C coupling const, Hz	internuclear distance, \AA^a
C_1 - C_6	11.6	1.67
C_1 - C_7	36.7 ± 0.1	1.53
C_3 - C_4	28.6 ± 0.1	1.55
C_4 - C_5	30.6	1.53
C_5 - C_6	59.1 ± 0.1	1.36

^aFrom 6-31g//6-31g calculations with C_s symmetry enforced on nortricycyl structure.

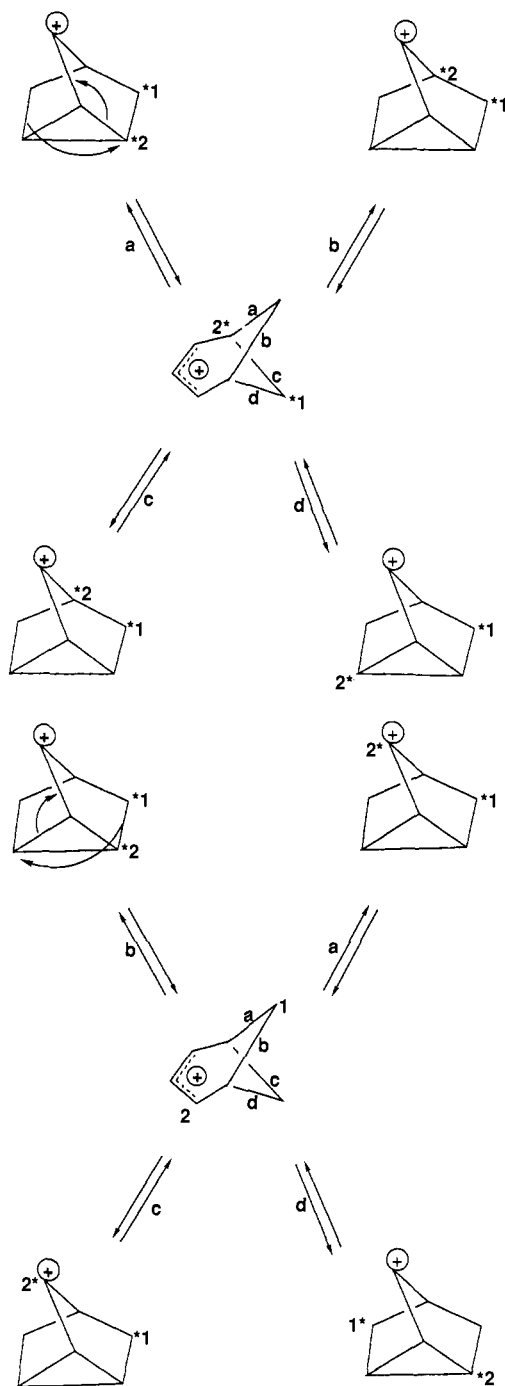
The fastest process involves skeletal rearrangement with no hydride shifts and can be detected at $-70\text{ }^{\circ}\text{C}$; a slower rearrangement involves a 1,2-hydride shift and occurs rapidly at $-50\text{ }^{\circ}\text{C}$. A still slower process (possibly a 1,3-hydride shift) requires heating to $\sim 0\text{ }^{\circ}\text{C}$.

We believe that the fastest process is a reversible rearrangement of the nortricycyl cation to the bicyclo[3.1.1]heptenyl cations⁶ (Scheme I). The rearrangement can proceed by migration of either the C_2 - C_3 bond (dilabeled) or the C_1 - C_7 bond (unlabeled) and therefore gives rise to two intermediate bicyclo[3.1.1]heptenyl cations differing only in ^{13}C positions. Ignoring a minor ^{13}C isotope effect, there is essentially an equal probability for any of the four identical bonds to migrate back and re-form the nortricycyl cation in both structures. This gives rise to four products in equal amounts. In addition to the C_2 - C_3 di- ^{13}C -labeled species (starting material), the C_1 - C_3 , C_3 - C_4 , and C_3 - C_5 di- ^{13}C -labeled cations are generated. These four cations (differing only by ^{13}C labeling) are sufficient to interpret the changes occurring at $-70\text{ }^{\circ}\text{C}$ in the ^{13}C NMR (and corresponding changes in the ^2H NMR, as well as ^1H NMR) spectra.

The original C_2 - C_3 di- ^{13}C -labeled material is still present and characterized by splitting due to coupling between C_2 and C_3 . After the fastest rearrangement process has come to equilibrium at $-70\text{ }^{\circ}\text{C}$, the C_1 - C_3 di- ^{13}C -labeled species contributes resonances

(6) Vogel, P.; Delseth, R.; Quarroz, D. *Helv. Chim. Acta* **1975**, *58*, 508. The C_7H_9 allylic cation was postulated as a possible intermediate in the acetolysis of *endo*-5-norbornen-2-yl brosylate (but no experimental evidence was found to support its presence in studies on the solvolysis of the 2-deuterio analog).

Scheme I



for both C_1 and C_3 , of course, without ^{13}C - ^{13}C coupling. This accounts for enlarged unsplit peaks for both C_2 and C_3 . The C_3 - C_4 di- ^{13}C -labeled species is responsible for the appearance of one of the new signals when the original di- ^{13}C -labeled cation is warmed to -70°C . It also requires that the resonance for C_4 be a doublet (coupled to C_3) as is seen in the ^{13}C NMR spectrum. The C_3 - C_5 di- ^{13}C -labeled species is needed to explain the appearance of the new singlet in the ^{13}C NMR spectrum corresponding to C_5 .

The presence of these four cations in essentially equal amounts accounts for the integration results of the inverse-gated decoupled spectra. First, C_3 (C_7) is not involved in this rearrangement process and therefore maintains its initial intensity throughout the scrambling process. Second, by summing up the contributions from the four cations at equilibrium, the relative intensity ratio of $C_3/C_7:C_2/C_1:C_4:C_5$ is 4:2:1:1, respectively, as is found experimentally. Finally, C_6 is not involved in this scrambling process, since no C_6 signal appears in the ^{13}C NMR spectrum when the nortricyclyl-2,3- $^{13}\text{C}_2$ cation is warmed at -50°C .

Table II. Relative Energies (kcal/mol) for Calculated Cation Geometries: Geometry Optimized (At Same Basis Set)

cation	sto-3g	3-21g	4-31g	6-31g
nortricyclyl ^a	0.0	0.0	0.0	0.0
allylic ^b	8.0	-1.0	-4.4	-4.6

^aWith C_s symmetry imposed. ^bWith C_{2v} symmetry imposed.

Table III. Relative Energies (kcal/mol) for Cations at 6-31g Geometry: Single Point Energy Calculation

cation	6-31g*	mp2	mp3
nortricyclyl ^a	0.0	0.0	0.0
allylic ^b	0.7	7.4	5.7

^aWith C_s symmetry imposed. ^bWith C_{2v} symmetry imposed.

The formation of these isotopically different di- ^{13}C -labeled nortricyclyl cations demands that at -70°C , C_2 (along with accompanying proton) must scramble with C_1 , C_4 , and C_5 . This, once again, exactly fits the spectroscopic ^2H NMR observations and the proton magnetization transfer results if no C-H(D) bonds are broken in the fastest process. First, no deuteriums on C_3/C_7 are exchanged at -70°C , as is shown by ^2H NMR spectroscopy in the isotopic perturbation study with 3,3-dideuterionortricyclyl cation. Second, deuterium on C_4 and C_5 must appear simultaneously when 2-deuterionortricyclyl cation is warmed to -70°C , as is seen experimentally. Third, the deuterium in 5-deuterionortricyclyl cation must first migrate to the C_1/C_2 position and then, after a second time through the scrambling cycle, from C_1/C_2 to the position at C_4 , as is seen in the ^2H NMR spectra at -70°C .

Results from ab initio calculations (Tables II and III) indicate that the allylic cation is a possible intermediate in the rearrangement process in nortricyclyl cation. The calculated energy difference between the two structures is quite basis set dependent. At the higher levels of geometry optimized calculations, the relative energies for the two structures are inverted with respect to experimental finds (and lower level calculations). Introduction of polarization functions and electron correlation is indicated. Once added, the allylic cation is properly found to be several kilocalories/mole higher in energy than the nortricyclyl cation.

In order to account for the eventual appearance of C_6 in the ^{13}C NMR spectrum at -50°C as well as the scrambling of the exo deuterium on C_3/C_7 to all other positions simultaneously (as seen in the ^2H NMR spectrum at -50°C), a C-D(H) bond must be broken and re-formed (Scheme II), and this must be a slower process than the rearrangement via bicyclo[3.1.1]heptenyl cation. The hydride shift results in the interchange of C_1 with C_4 , C_2 with C_3 , and C_5 with C_6 or C_1 with C_7 , C_2 with C_4 , and C_5 with C_6 . This therefore, involves all of the carbons and seven of the nine hydrogens (deuteriums) in the scrambling process.

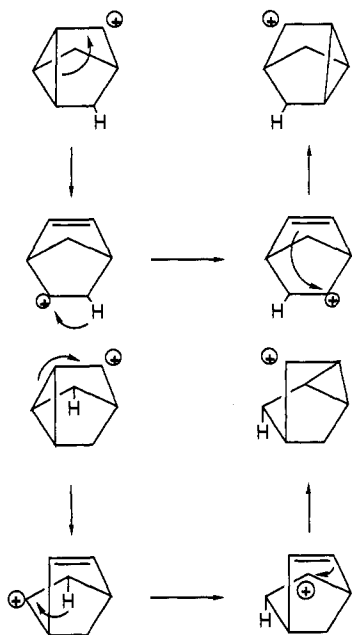
The final two hydrogens (deuteriums) don't become involved in the scrambling process until the cation is warmed to $\sim 0^\circ\text{C}$, and by this point any process which migrates this hydrogen (deuterium) to any other positions will lead to total scrambling of the carbons and hydrogens in the nortricyclyl cation. Such a process could be a 1,3-hydride shift, from the exo proton (deuteron) on C_3/C_7 to C_5 .

With complete scrambling, ^{13}C - ^{13}C coupling constants between all adjacent carbon pairs are measurable (Table I). The particularly small value for the C_1 - C_6/C_2 - C_6 pair indicates a longer than usual or stretched C-C bond, and the particularly large value for the C_5 - C_6 pair indicates a C-C bond containing substantial double bond character. These experimentally based finds are supported by 6-31//6-31g level quantum mechanical calculations (Table I).

Conclusions

We believe that the small splitting in the ^{13}C NMR spectrum of norbornenyl-nortricyclyl cation described in the deuterium isotopic perturbation experiment results from an intrinsic isotope shift; the frequency of C_2 is shifted upfield by the deuteriums at C_3 . Even a small amount of a rapidly equilibrating pair of species

Scheme II



like the norbornenyl cation would be expected to produce a much larger and temperature-dependent splitting. We conclude that the system is therefore essentially a static one, with no more than about 1% equilibrating species.

It must be recognized that the question of whether the ion is rapidly equilibrating or static is quite distinct from considerations of the bonding and charge distribution in the one or more structures which might be present. Experimentally obtained ^{13}C - ^{13}C coupling constants and quantum mechanical calculations at the 6-31g//6-31g level suggest that the C_5 - C_6 bond is quite short (containing substantial double-bond character) and the C_1 - C_6 and C_2 - C_6 bonds are quite long. However, ^{13}C - ^{13}C coupling constants within cyclopropanes are normally smaller than those for other carbon-carbon single bonds, and bonds external to cyclopropanes generally result in larger coupling constants.⁷ Therefore, although there must be a single structure with the symmetry of nortricycyl cation, considerable delocalization of the charge and bonding may well be present.

At temperature above -70°C , partial carbon scrambling in the nortricycyl system is detected in the ^{13}C NMR spectrum of the 2,3-di- ^{13}C -labeled cation (as well as in the ^2H NMR spectrum of deuteriated cations). The scrambling of atoms is achieved by skeletal rearrangements taking place via the bicyclo[3.1.1]heptenyl cation. The scrambling of *all* atoms is completed by subsequent slower hydride shifts, detected at -50 and 0°C .

Experimental Section

3,3-Dideuterio-5-norbornen-2-yl Chloride and 3,3-Dideuterionortricycl-5-yl Chloride. 5-Norbornen-2-ol (19 g, dissolved in 500 mL of CH_2Cl_2) is quickly added to a 3000-mL three-necked round-bottomed flask containing dry pyridine (163 g), CH_2Cl_2 (1100 mL), and dried chromium trioxide (103 g, added slowly with thorough stirring). After 15 min of stirring, the reaction mixture is filtered through Celite. The filtrate is washed with 5% aqueous KOH solution, 5% aqueous HCl solution, saturated NaHCO_3 solution, and saturated NaCl solution and dried by filtration through anhydrous Na_2SO_4 . Distillation removes solvents and yields solvents and yields 5-norbornen-2-one (16.9 g, 90%), bp 50 - 55°C at 10 torr.

A mixture of 5-norbornen-2-one (8 g), sodium methoxide (24 g), D_2O (102 mL), and CH_3OD (25 mL) is heated in a 250-mL closed container at about 100°C for 16 h with constant stirring. The organic material is extracted with ether, washed with D_2O , filtered through anhydrous Na_2SO_4 , and distilled to yield 3,3-dideuterio-5-norbornen-2-one⁸ (4.8 g, 59%), bp 50 - 55°C at 10 torr.

3,3-Dideuterio-5-norbornen-2-one (2 g), methanol (5 mL), and acetic acid (0.2 mL) are placed in a 50-mL round-bottomed flask and cooled by an ice bath. NaBH_4 (0.35 g in 5 mL of H_2O) is slowly added, and the mixture is allowed to stir at room temperature for 2 h. By the addition of 4 N H_2SO_4 , the pH of the solution is brought to 6. The product is extracted with ether and dried by Na_2SO_4 filtration, and the solvents are removed by distillation. The remainder (1.7 g) is placed in a flask with triphenylphosphine (14.6 g) and CCl_4 (65 mL) and refluxed for 16 h. Pentane is added to the cooled solution until precipitate formation ceased. After removal of the precipitate, distillation yielded a mixture of 3,3-dideuterio-5-norbornen-2-yl chloride and 3,3-dideuterionortricycl-5-yl chloride (2.8 g total, 68% from the ketone), bp 64 - 67°C at 10 torr.⁹

3-Deuterio-5-norbornen-2-yl Chloride and 3-Deuterionortricycl-5-yl Chloride. Starting from 5-norbornen-2-ol, the preparation of the monodeuteriated (exo) chlorides is the same as that for the dideuteriated chlorides, except that the reaction time for the deuterium incorporation is 2.5 h instead of 16 h and the reaction is run at room temperature instead of 100°C .

2-Deuterio-5-norbornen-2-yl Chloride and 2-Deuterionortricycl-5-yl Chloride. Starting from 5-norbornen-2-ol, the preparation of the monodeuteriated chlorides is the same as that for the dideuteriated chlorides, except that no H/D exchange is performed on the ketone; rather, 5-norbornen-2-one is reacted with NaBD_4 , in place of NaBH_4 .

5-Deuterionortricycl-5-yl Chloride. Norbornadiene (103 g), acetic acid (70 mL), and BF_3 -etherate (2.5 mL) are placed in a flask and gradually warmed to about 100°C , under a stream of nitrogen, for 6 h. Once cooled, the reaction mixture is diluted with ether and successively washed with 1.5 M Na_2CO_3 solution and water. Distillation yields nortricyl-5-yl acetate (136 g, 80% with minor traces of norbornen-2-yl acetate), bp 74 - 75°C at 8 torr.

Nortricycl-5-yl acetate (99 g) is added to anhydrous methanol (500 mL), containing sodium metal (1 g, introduced slowly). The reaction mixture is heated to reflux for 4 h. Methanol is removed by distillation. A portion of the residue (80 g, dissolved in 400 mL of acetone) is introduced into a three-necked 1000-mL flask and cooled by an ice bath. Keeping the reaction mixture temperature solution below 20°C , chromic acid solution (59 g CrO_3 , 70 mL of water, and 43 mL of concentrated H_2SO_4) is added and the entire mixture is allowed to stir at room temperature for 3 h. NaHSO_3 is added in small portions until the upper layer is colorless. The product is then extracted with petroleum ether (35 - 60°C). The organic layer is washed with saturated NaHCO_3 and saturated NaCl and filtered through NaHSO_4 . Distillation yields nortricycyl-5-one, bp 59 - 61°C at 8 torr. The ketone is then taken on to the deuteriated alcohol with NaBD_4 and the alcohol converted to 5-deuterionortricycl-5-yl chloride with $\text{PPh}_3/\text{CCl}_4$, as outlined previously.

Norbornen-2-yl-2,3- $^{13}\text{C}_2$ Chloride and Nortricycl-5-yl-2,3- $^{13}\text{C}_2$ Chloride. $\text{Ba}^{13}\text{CO}_3$ (20 g, 98% enriched) and magnesium powder (49.2 g, 70-80 mesh) are intimately mixed by grinding with mortar and pestle and loaded in 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 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 is applied (from the dropping funnel top) as the water is allowed to drop onto the barium carbide. After all the water (200 mL) had been added, the solution is brought to boil with a heat gun for 20 min. The trap containing the fluffy white $^{13}\text{C}_2$ 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%).¹⁰ ^{13}C NMR acetone- d_6 δ 73.4 ($^1J^{\text{H}-^{13}\text{C}} = 297.8$, $^2J^{\text{H}-^{13}\text{C}} = 93.0$ Hz).

$^{13}\text{C}_2$ Acetylene (35 mmol) is transferred on the vacuum line to a 1000-mL round-bottomed 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 vinyl-1,2- $^{13}\text{C}_2$ acetate (1.1 g, 80%), bp 72 - 74°C .

(7) (a) Levy, G.; Nelson, G. *CMR Spectroscopy*; Wiley: New York, 1980. (b) Stothers J. B. *Carbon-13 NMR*; Academic: New York, 1972.

(8) Jerkunica, J. M.; Brocic, S.; Sunko, D. E. *Tetrahedron Lett.* **1965**, 49, 4465.

(9) For typical reaction conditions, see: Weiss, R. G.; Snyder, E. I. *J. Org. Chem.* **1971**, 36, 403-406.

(10) Roberts, J. D.; Lee, C. C.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1954**, 76, 4501. Walker, G. W. Ph.D. Thesis, Yale University, 1983.

^{13}C NMR (CDCl_3) δ 142.0 ($^1J^{\text{H}-^{13}\text{C}} = 189.0$ Hz), 96.7 ($^1J^{\text{H}-^{13}\text{C}} = 161.5$, $^2J^{\text{H}-^{13}\text{C}} = 150.0$, $J^{^{13}\text{C}-^{13}\text{C}} = 82.8$ Hz).

Vinyl-1,2- $^{13}\text{C}_2$ 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, 5-norbornenyl-2,3- $^{13}\text{C}_2$ acetate (1.8 g) is produced, bp 82–83 °C at 17 torr: ^{13}C NMR (CDCl_3) δ 74.8 ($^1J^{\text{H}-^{13}\text{C}} = 158.5$ Hz), 34.8 ($^1J^{\text{H}-^{13}\text{C}} = 134.5$, $J^{^{13}\text{C}-^{13}\text{C}} = 44.1$ Hz).

5-Norbornenyl-2,3- $^{13}\text{C}_2$ acetate is converted to 5-norbornen-2,3- $^{13}\text{C}_2$ -ol by Na/methanol hydrolysis in 72% yield: ^{13}C NMR (methanol- d_4) δ 19.4 ($^1J^{\text{H}-^{13}\text{C}} = 132.9$ Hz), 55.03 ($^1J^{\text{H}-^{13}\text{C}} = 148.5$, $J^{^{13}\text{C}-^{13}\text{C}} = 43.6$ Hz). 5-Norbornen-2,3- $^{13}\text{C}_2$ -ol is transformed into 5-norbornen-2-yl-2,3- $^{13}\text{C}_2$ chloride and nortricycl-5-yl-2,3- $^{13}\text{C}_2$ chloride by $\text{PPh}_3/\text{CCl}_4$, as previously outlined. 5-Norbornen-2-yl-2,3- $^{13}\text{C}_2$ chloride and nortri-

cycl-5-yl-2,3- $^{13}\text{C}_2$ chloride can be separated by preparative GC with a UV-101 column at 145 °C: ^{13}C NMR (CDCl_3) norbornenyl chloride δ 58.4 ($^1J^{\text{H}-^{13}\text{C}} = 161.8$ Hz), 38.2 ($^1J^{\text{H}-^{13}\text{C}} = 137.7$, $J^{^{13}\text{C}-^{13}\text{C}} = 42.7$ Hz), *endo/exo*-nortricyclyl chloride 30.1, 11.1; 31.5, 13.7, ($J^{^{13}\text{C}-^{13}\text{C}} = 39.5$ Hz).

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$(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{FeCH}_2\text{S}^+(\text{CH}_3)_2\text{BF}_4^-$: A Methylene Transfer Reagent for the Direct Cyclopropanation of Alkenes¹

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Abstract: $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{S}^+(\text{CH}_3)_2\text{BF}_4^-$ (**5a**, Cp = η^5 -cyclopentadienyl) is readily prepared by the reaction of the ferrate $\text{Na}^+[\text{Cp}(\text{CO})_2\text{Fe}]^-$ with chloromethyl methyl sulfide to give the alkylation product $\text{Cp}(\text{CO})_2\text{FeCH}_2\text{SCH}_3$ (**4**) as an intermediate that need not be isolated but which is treated directly with various methylating agents (e.g. $(\text{CH}_3)_3\text{O}^+\text{BF}_4^-$, $(\text{CH}_3\text{O})_2\text{CH}^+\text{BF}_4^-$, FSO_3CH_3 , etc.) to give **5a**. This salt is an exceptionally stable organometallic reagent that has been characterized spectroscopically as well as by X-ray diffraction. Complex **5a** undergoes direct reaction with a wide range of alkenes to give cyclopropanes in a synthetically useful manner. Several aspects of this cyclopropanation procedure have been probed in order to gain a more detailed understanding of this reaction.

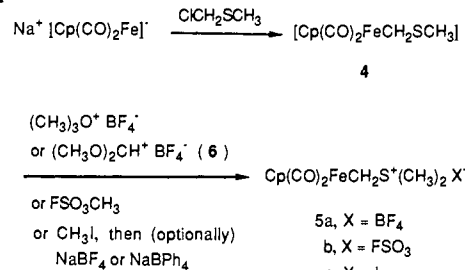
The cyclopropane ring system is seen as an important structural feature among many classes of naturally occurring compounds.³ Also, because of various cleavage reactions and rearrangements in which they participate, cyclopropanes frequently serve as valuable synthetic intermediates leading to other ring systems or acyclic products. Consequently, a large number of methods have been developed for the synthesis of cyclopropanes. The vast majority of these methods may be placed in either of two broad

(1) Taken in part from the Ph.D. Dissertations of (a) S.B. (1979) and (b) E.J.O. (1984), State University of New York at Stony Brook.

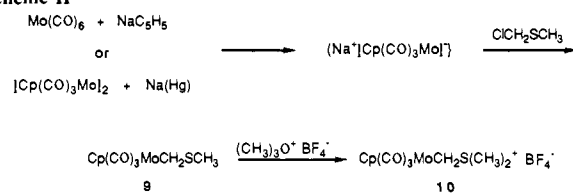
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(3) For some reviews concerned with the occurrence, preparation, and reactions of cyclopropanes see: (a) Wendisch, D. In *Methoden der Organischen Chemie (Houben-Weyl)*; Müller, E., Ed.; Georg Thieme Verlag: Stuttgart, 1971; Vol. IV, Part 3, pp 15–673. (b) Simmons, H. E.; Cairns, T. L.; Vladuchick, S. A.; Hoiness, C. M. *Org. React. (N.Y.)* **1973**, *20*, 1. (c) Ferguson, L. N. *Highlights of Alicyclic Chemistry*; Franklin: Palisade, NJ, 1973; pp 21–271. Ferguson, L. N.; Paulson, D. R. *Ibid.* **1977**; Part 2, pp 89–109. (d) Boyle, P. H. In *Rodd's Chemistry of Carbon Compounds*, 2nd ed.; Ansell, M. F., Ed.; Elsevier: Amsterdam, 1974; Vol. IIA, Suppl, pp 9–47 and the earlier volumes of this series. (e) Yanovskaya, L. A.; Dombrovskii, V. A. *Russ. Chem. Rev. (Engl. Transl.)* **1975**, *44*, 154. (f) Burke, S. D.; Grieco, P. A. *Org. React. (N.Y.)* **1979**, *26*, 361. (g) Wenkert, E. *Acc. Chem. Res.* **1980**, *13*, 27. (h) Moss, R. A. *Acc. Chem. Res.* **1980**, *13*, 58. (i) Freidlina, R. Kh.; Kamysheva, A. A.; Chukovskaya, E. Ts. *Russ. Chem. Rev. (Engl. Transl.)* **1982**, *51*, 368. (j) McQuillin, F. J.; Baird, M. S. *Alicyclic Chemistry*, 2nd ed.; Cambridge University Press: Cambridge, 1983; pp 92–112. (k) Moody, C. J. In *Organic Reaction Mechanisms 1984*; Knipe, A. C., Watts, W. E., Eds.; Wiley: Chichester, 1986; Chapter 6 and the earlier volumes of this series. (l) Hudlicky, T.; Kutchan, T. M.; Naqvi, S. M. *Org. React. (N.Y.)* **1985**, *33*, 247. (m) Larock, R. C. *Organomercury Compounds in Organic Synthesis*; Springer-Verlag: Berlin, 1985; pp 327–380. (n) Aratani, T. *Pure Appl. Chem.* **1985**, *57*, 1839. (o) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919. (p) Brookhart, M.; Studabaker, W. B. *Ibid.* **1987**, *87*, 411.

Scheme I



Scheme II



categories: (1) addition of carbenes, carbenoids, or related species to alkenes and (2) intramolecular coupling or alkylation reactions. Certain aspects of these approaches are shared with a number of reagents that undergo nucleophilic addition to suitably activated alkenes followed by intramolecular alkylation, either with or without site equilibration of the initially formed carbanionic intermediates. Included in this description are the use of sulfonium ylides⁴ among many other species.⁵