Corner versus Edge Protonation of Cyclopropane

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Acid-catalyzed addition of methanol to **1** occurs by rupture of the internal carbon–carbon bond of the cyclopropane to give **2** with both retention and inversion at the site of electrophilic attack (**4**:**5**, 1.3:1.0). Nucleophilic attack occurs with inversion without relaxation of the corner- and edge-protonated cyclopropanes to a secondary cation.

Introduction

Cyclopropanes are useful intermediates in synthesis, and therefore it is important to understand the factors which affect the regio- and stereochemistry of the ring opening. Addition of H^+ to cyclopropanes generally occurs with inversion of configuration at the site of electrophilic attack,[1] although examples of retention have been reported.[2] For monosubstituted cyclopropanes, the regiochemistry of electrophilic addition is rationalized by a modified Markovnikov rule whereby the carbon–carbon bond which is cleaved is that between the most and least substituted carbons.[1,3] For disubstituted cyclopropanes, rupture of the most substituted carbon–carbon bond is however generally observed.[1,3] The competition between electrophilic addition to a cyclopropane and alkene also needs to be understood for these two functional groups within a molecule to be selectively elaborated.

The inclusion of a cyclopropyl moiety in a polycyclic skeleton can often allow definitive elucidation of the regio- and stereochemical outcome of the reaction at the cyclopropyl moiety with an electrophile.[3] Examples of electrophilic addition to tricyclo[3.2.1.$0^{2,4}$]octanes and -oct-6-enes have been reported[1] to result from H^+/D^+ addition to the most substituted (C2–C4) bond with inversion of configuration at the site of electrophilic attack. The use of unsubstituted symmetrical tricyclic systems which contain cyclopropane along with alkene moieties results in simplification of both orbital/electronic and steric factors and allows the regio- and stereochemical aspects of the reaction to be determined.[2,4]

Results and Discussion

We report studies to determine the regio- and stereochemistry of electrophilic addition of H^+/D^+ to *exo*-tricyclo[3.2.2.$0^{2,4}$]non-6-ene (**1**). Reaction with a catalytic amount of *p*-toluenesulfonic acid (PTSA) in dry methanol at 80 °C for 21 days gave 2-*exo*-methoxybicyclo[3.2.2]non-6-ene (**2**) (Figure 1).

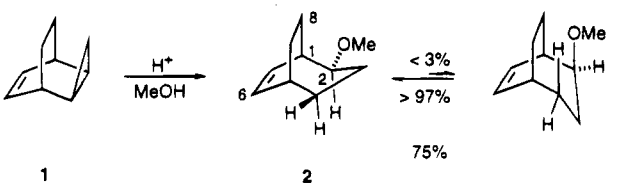

Figure 1. Reaction of *exo*-tricyclo[3.2.2.$0^{2,4}$]non-6-ene (**1**) with H^+-MeOH.

The identity of **2** was established[5] from HMQC-DEPT and DQCOSY experiments which established the one-bond $^1H-^{13}C$ connectivities and many of the $^1H-^1H$ connectivities, respectively. A DEPT135 experiment showed the carbons at 30.3 (C4) and 30.6 (C3) ppm to be methylene carbons and the ^{13}C resonance at 30.5 ppm to be that of a methine carbon.[6] The presence of a **C**HOMe group was determined from the chemical shift of C2 (79.5 ppm) and H2 (3.08 ppm).[7,8] The absence of a significant coupling of H1 to H2 determined an axial orientation of H2[9] which was confirmed from the coupling constants of H2 to $H3_{endo}$ (1.99 ppm, $^3J_{2,3endo} = 5.3$ Hz) and $H3_{exo}$ (1.79 ppm, $^3J_{2,3exo} = 10.4$ Hz) which are consistent with a *trans* arrangement of H2 and $H3_{exo}$. A 1D-TOCSY, performed by irradiation of H2, allowed identification of the $H3_{exo}$ multiplet (d of d of t) and also allowed confirmation of the size of the coupling constants of $H3_{exo}$ to H2 and determination of the coupling constants of $H3_{exo}$ to $H4_{endo}$ and $H4_{exo}$ ($^3J_{3exo,2} = {}^3J_{3exo,4endo} = 9.8$ Hz, $^3J_{3endo,4exo} = 6.0$ Hz). The 1D-TOCSY also allowed determination of the

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(2) Hendrickson, J. B.; Boeckman, R. K. *J. Am. Chem. Soc.* **1969**, *91*, 3269.

(3) Coxon, J. M.; Steel, P. J.; Whittington, B. I. *J. Org. Chem.* **1989**, *54*, 1383. Coxon, J. M.; Steel, P. J.; Whittington, B. I. *J. Org. Chem.* **1989**, *54*, 3702. Coxon, J. M.; Steel, P. J.; Whittington, B. I. *J. Org. Chem.* **1990**, *55*, 4136. Coxon, J. M.; Steel, P. J.; Whittington, B. I.; Battiste, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 2988. For reaction with bromine, see: Burritt, A.; Coxon, J. M.; Steel, P. J.; Whittington, B. I. *J. Org. Chem.* **1995**, *60*, 2812.

(4) A number of reactions involving H^+ addition to compounds containing a tricyclo[3.2.2.$0^{2,4}$]non-6-ene carbon skeleton have been reported with both modified Markovnikov and modified *anti*-Markovnikov addition being observed. However, the unsymmetrical nature of the compounds studied complicates the analysis of orbital effects on the trajectory of electrophilic addition to the cyclopropane ring.[2] Zimmerman, M. P.; Li, H.-T.; Duax, W. L.; Weeks, C. M.; Djerassi, C. *J. Am. Chem. Soc.* **1984**, *106*, 5602. McManus, L. D.; Rogers, N. A. J. *Tetrahedron Lett.* **1969**, 4735. Müller, E. *Chem. Ber.* **1976**, *109*, 3793.

(5) 2-*exo*-Hydroxybicyclo[3.2.2]non-6-ene and 2-*endo*-hydroxybicyclo-[3.2.2]non-6-ene have been reported, but the NMR data have not been published. Berson, J. A.; Luibrand, R. T.; Kundu, N. G.; Morris, D. G. *J. Am. Chem. Soc.* **1971**, *93*, 3075.

(6) An HMBC showed correlations from H2 (3.08 ppm) to carbons C7 (131.1 ppm) and C8 (20.3 ppm). Correlations from H7 to C1 (36.1 ppm), C8, and C6 (138.5 ppm) and from H6 to C9 (24.3 ppm) and C1 in conjunction with the DQCOSY experiment established the bicyclo-[3.2.2]non-6-ene carbon skeleton.

(7) The methoxy group appeared as a singlet at 3.30 ppm in the ^1H NMR spectrum with the corresponding ^{13}C resonance at 56.0 ppm in the ^{13}C NMR spectrum.

(8) Difference NOE experiments were of little help in the assignment of the stereochemistry at C4 due to the similarity of the chemical shifts of the protons attached to C3 (1.79 and 1.99 ppm) with those of the C8 (1.57 and 2.03 ppm) and C9 (1.58 and 1.72 ppm) methylene groups.

(9) This has also been observed for similar compounds: 2-*exo*-bromo-4-*exo*-methoxybicyclo[3.2.2]non-6-ene and 2-*exo*-4-*exo*-dimethoxybicyclo-[3.2.2]non-6-ene, which have an *endo* orientation of H2 and show little or no coupling to the bridgehead proton H1. Coxon, J. M.; Steel, P. J.; Burritt, A.; Whittington, B. I. *Tetrahedron* **1995**, *51*, 8057. Blunt, J. W.; Burritt, A.; Coxon, J. M.; Steel, P. J. *Magn. Reson. Chem.* **1995**, in press.

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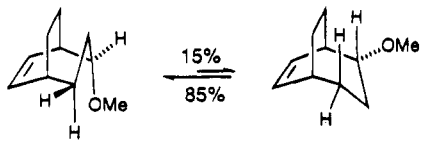
Table 1. Calculated and Experimental Coupling Constants of 2 and 3

	vicinal coupling constants (Hz)		
compd	1,2	2,3-*exo*	2,3-*endo*
2 (obsd)	<1.0	10.4	5.3
2 (calcd)	1.4	10.4	5.3
3 (calcd)	5.2	3.7	4.2

geminal coupling constant of $H3_{exo}$ to $H3_{endo}$ ($^2J_{3exo,3endo}$ = 13.3 Hz) and established the assignment of the protons of the C4 methylene group.

The stereochemistry at C2 was established by comparison of the observed coupling constants with those calculated from a grid conformational search of **2** and the epimeric structure of 2-*endo*-methoxybicyclo[3.2.2]non-6-ene (**3**) using the program BKM[10] incorporating the MM2 force field. The calculations predict the *exo* conformation of the bridge, with C3 *syn* to the ethano bridge, is populated >97% for **2** and ca. 85% for **3**.



3

The Boltzmann averaged coupling constant of H1 to H2 in each was calculated using BKM which implements an empirical generalization of the Karplus equation developed by Haasnoot et al.[11] for the distribution of the conformers within a 12.5 kJ mol^{-1} energy window (**2**, $^3J_{1,2}$ = 1.4 Hz; **3**, J = 5.2 Hz) (Table 1). The configuration of H2 (experimental $^3J_{1,2}$ < 1 Hz) is therefore assigned as *endo* which requires an *exo* orientation of the C2 methoxy group. The exo conformation of the three-membered bridge is more favorable. The larger calculated coupling constant of H1 to H2 predicted for **3** (5.2 Hz) compared to that for **2** (1.4 Hz) along with a comparison of the observed[12] and calculated values for the $^3J_{2,3endo}$ and $^3J_{2,3exo}$ couplings shows good agreement for structure **2** but significant deviation, especially for $^3J_{2,3exo}$, from those values calculated for **3**. Further support for the assignment in the configurational at C2 in **2** comes from a comparison of the ^{13}C NMR spectrum of **2** with that of 2-*exo*-bromo-4-*exo*-methoxybicyclo[3.2.2]non-6-ene[13] and 2-*exo*-4-*exo*-dimethoxybicyclo[3.2.2]non-6-ene[13] which both have a similar *exo* methoxy substituent. Specifically the chemical shifts of C6 (133.3 ppm) in 2-*exo*-bromo-4-*exo*-methoxybicyclo[3.2.2]non-6-ene and C6/C7 (132.8 ppm) in 2-*exo*-4-*exo*-dimethoxybicyclo[3.2.2]non-6-ene compares favourably with the analogous carbon, C7, (131.1 ppm) in **2**.

The chemical shift of H8*syn* (2.03 ppm) is also consistent with an *exo* orientation of the C2 methoxy group which would be expected to deshield this proton in structure **2**.

To establish the trajectory of electrophilic attack on the cyclopropane ring, the reaction of **1** with a catalytic amount of PTSA was repeated using methanol-d_1 as solvent.[14] The peak corresponding to the major product(s) was collected by preparative GLC and shown from a ^{2}H NMR spectra to be a mixture of 4-*exo*-deuterio-2-*exo*-methoxybicyclo[3.2.2]non-6-ene (**4**) (40%) and 4-*endo*-deuterio-2-*exo*-methoxybicyclo[3.2.2]non-6-ene (**5**) (31%) in a ratio of 1.3:1.0 (Figure 2).

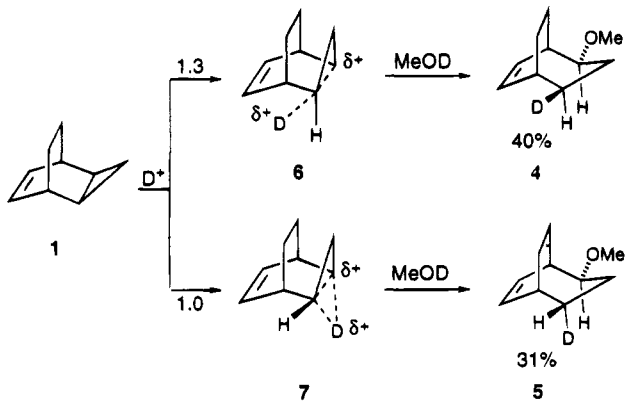


Figure 2. Reaction of *exo*-tricyclo[3.2.2.0^{2,4}]non-6-ene (**1**) with D$^+$-MeOD.

The ^{1}H NMR spectrum of the mixture of **4** and **5** appeared nearly identical with that of **2**.[15] The ^{13}C NMR spectrum of the mixture of deuterated products showed 13 signals due to deuterium isotope shift effects.[16] Signals at 137.9, 131.0$_8$, and 131.1$_1$ ppm in the ^{13}C NMR spectrum with the corresponding protons at 6.21 and 5.97 ppm in the ^{1}H NMR spectrum established the presence of the alkene groups. The presence of a ^{13}C signal at 78.8 ppm and a proton at 2.98 ppm confirmed the presence of a **CH**OMe group. The methoxy group was evident as a singlet in the ^{1}H NMR spectrum at 3.20 ppm with the methoxy carbon resonance at 55.4 ppm in the ^{13}C NMR spectrum. The bridgehead protons H1 and H5 were evident at 2.42 (H1) and 2.28 (H5) ppm and the C1 bridgehead carbon at 35.9 ppm in the ^{13}C NMR spectrum. The C9 carbons of **4** and **5** appeared at 24.4 ppm and the C8 carbons at 20.1 and 20.0 ppm.[17] The appearance of four carbons in the range 30.0 ≃ 30.3 ppm was attributed to C3 and C4 of **4** and **5**, and one signal showing line broadening, which was identified as a methine carbon from a DEPT135 experiment, was assigned to C5 of **4** and **5**.[18] The chemical shifts of $H4_{exo}$ of **5** and $H4_{endo}$ of **4** (1.59 and 1.46 ppm, respectively) were identified from a 1D-TOCSY experiment on irradiation of H2. The ^{2}H

(10) BAKMDL (BKM), Version KS 2.99, 1992.
(11) Haasnoot, C. A. G.; De Leeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2783.
(12) The observed values shown for the coupling of H2 to $H3_{endo}$ and $H3_{exo}$ were extracted from the H2 multiplet.
(13) Burritt, A. Ph.D. Thesis, University of Canterbury, Christchurch, New Zealand, 1993.
(14) GLC analysis of the products showed three peaks in a similar ratio to that observed for the reaction in methanol (71%, 16%, and 13%).
(15) The chemical shift values reported above for **4** and **5** were determined with CCl_4 as the NMR solvent and those of **2** in $CDCl_3$. The ^{1}H and ^{13}C NMR spectra of **4** and **5** were also obtained in $CDCl_3$ for comparison to those of **2**. The ^{1}H and ^{13}C NMR spectra of **2** were also run in CCl_4 for comparison to those of **4** and **5**.
(16) Künzer, H.; Cottrell, C. E.; Paquette, L. A. *J. Am. Chem. Soc.* **1986**, *108*, 8089. Aydin, R.; Frankmölle, W.; Schmalz, D.; Günther, H. *Magn. Reson. Chem.* **1988**, *26*, 408.
(17) The appearance of carbons C7 and C8 as separate signals for **4** and **5** reflects the dependence of the four-bond isotope shift effects, whereas C6 and C9, which are in a three-bond relationship to the deuterium atoms of C4, do not show resolvable isotope shift effects since three bond isotope shift effects are not stereochemically dependant. Hence both $D4_{exo}$ and $D4_{endo}$ of **4** and **5**, respectively, would be expected to show similar isotope shift effects on C6 and C9.[18]
(18) The chemical shifts of C3, C4, and C5 of **4** and **5** were not well resolved in the ^{13}C NMR due to their similar chemical shifts and the low intensity of the C4 triplet. Three ^{13}C signals arising from C3 and C4 of **4** and **5** were presumed due to the weak triplet signals of C4 (which were not observed separately) overlapping with each other and/or the C3 and C5 signals.

NMR spectrum[19] of the two deuterio isomers showed two signals (1.80 and 1.65 ppm) in a ratio of 1.3:1.0 (**4**:**5**).[20]

The products obtained from addition of methanol to **1** are consistent with both edge and corner addition of the electrophile to the C2–C4 bond of the cyclopropane ring, which results in retention and inversion, respectively, at the site of electrophilic attack. The similarity of the ratio of **4** to **5** obtained suggests that the corner and edge trajectories have similar energies. This contrasts with the results reported for methanol addition to *exo*- and *endo*-tricyclo[3.2.1.$0^{2,4}$]octane and -oct-6-ene where electrophilic addition to the cyclopropane ring occurs exclusively with inversion.[21,1,3] Nucleophilic attack occurred with inversion to form products **4** and **5** which is consistent with the formation of corner- (**6**) and edge- (**7**) protonated intermediates without relaxation to a classical secondary cation (Figure 2).

For **1** no skeletal rearrangement is observed in contrast to the reaction of *exo*-tricyclo[3.2.1]oct-6-ene.[1,3] Since the major product does not result from rearrangement, it appears that either significant charge development at the carbon where nucleophilic capture takes place does not occur during protonation of the cyclopropane ring or that structural reorganization of the bicyclo[3.2.2]non-6-ene carbon skeleton is not as energetically facile as that of the corresponding bicyclo[3.2.1]oct-6-ene.

The observed products are consistent with an unusually facile competition of edge and corner attack of the electrophile at the most substituted cyclopropyl bond with nucleophilic capture occurring with inversion of conversion.

Conclusion

Acid-catalyzed addition of methanol to **1** occurs to the cyclopropane in preference to the double bond and results in cleavage of the most substituted carbon–carbon bond of the cyclopropane. Deuterium-labeling experiments show that electrophilic attack on the cyclopropyl ring occurs with both inversion and retention of configuration (1.3:1.0). The stereochemical assignment of the methoxy group in the product(s) was established by comparison of the observed coupling constants with those calculated from a Boltzmann distribution of conformers which accommodate the conformational flexibility of the three-carbon bridge. Nucleophilic capture of the resulting cation occurs with inversion of configuration before the edge- and corner-protonated cations have relaxed to a classical cation.

Experimental Section

NMR spectra were recorded with a 5 mm probe and at 300 and 75 MHz for ^{1}H and ^{13}C, respectively. ^{2}H NMR spectra were acquired unlocked at 46 MHz and were proton coupled. Chemical shifts are reported in ppm relative to tetramethylsilane. Experiments were generally recorded using standard pulse sequences and parameters available with the XL-300 or Unity 300 systems. Proton chemical shifts marked with a superscript asterisk were estimated from NOE or 2D-NMR experiments (DQCOSY, HMQC, or HMQC-DEPT experiments). Proton chemical shifts marked with a superscript hash mark (#) were determined from 1D- or 2D-TOCSY experiments. Mass spectra were recorded using a spectrometer directly coupled to a GLC instrument fitted with a Restex R_{tx}1 30 m x 0.32 mm capillary column. A programmed run was used for the GCMS (an initial temperature of 60 °C was held for 1 min and then the column temperature increased at the rate of 20 °C/min up to 260 °C) to ensure that the sample and all impurities passed through the column to the MS instrument. Analytical and preparative GLC were carried out with a 1.5% OV-17, 1.25% QF-1 Chromosorb W-packed column of 5 mm o.d. and 3.0 m length or a 1.5% OV-17, 1.95% QF-1 Chromosorb W-packed column of 10 mm o.d. and 2.5 m length.

Preparation of *exo*-Tricyclo[3.2.2.$0^{2,4}$]non-6-ene (1). *exo*-Tricyclo[3.2.2.$0^{2,4}$]non-6-ene (**1**) was synthesized by the literature procedure and identified by comparison of its ^{1}H NMR spectra with that reported.[22,23] **1**: colorless semisolid; bp 165–168 °C (lit.[23] bp 162–168 °C); ^{1}H NMR ($CDCl_3$) δ_H 6.50 (d of d, $^3J_{6,5} = {}^3J_{7,1} = 4.5$ Hz, $^4J_{6,1} = {}^4J_{7,5} = 2.9$ Hz, H6, H7), 2.64 (m, H1, H5), 1.39 (m, $H8_{syn}$, $H9_{syn}$), 1.02 (m, H2, H4), 0.86–0.98 (m, $H3_{exo}$, $H8_{anti}$, $H9_{anti}$), 0.58 (d of t, $^2J_{3endo,3exo} = 5.9$ Hz, $^3J_{3endo,2} = {}^3J_{3endo,4} = 7.3$ Hz, $H3_{endo}$); ^{13}C NMR ($CDCl_3$) δ_C 137.8 (C6, C7), 29.9 (C1, C5), 23.2 (C8, C9), 21.5 (C2, C4), 14.1 (C3); MS (C_9H_{12}) $M^{\bullet+}$ requires 120.0939, found 120.0934.

Reaction of *exo*-Tricyclo[3.2.2.$0^{2,4}$]non-6-ene (1) with a Catalytic Amount of PTSA in Methanol. A solution of **1** (305 mg, 2.54 mmol) and PTSA (30 mg, 0.16 mmol, 0.06 mol equiv) in dry methanol (3 mL) was heated in a sealed tube at 80 °C for 21 days. The methanol was removed under reduced pressure, the resulting brown oil taken up with pentane, washed with a saturated solution of sodium bicarbonate (3 mL) and water (3 mL), and dried over $MgSO_4$, and the solvent removed under reduced pressure to give a yellow oil (149 mg, ca. 39% recovery) which was shown by GLC analysis to contain three products. The major product, 2-*exo*-methoxybicyclo-[3.2.2]non-6-ene (**2**) (75%) was isolated by preparative GLC. The remaining two products (15% and 10%) were not identified. **2**: colorless oil; ^{1}H NMR ($CDCl_3$) δ_H 6.28 (t, $^3J_{6,5} = {}^3J_{6,7} = 8.1$ Hz, H6), 6.04 (t, $^3J_{7,1} = {}^3J_{7,6} = 8.4$ Hz, H7), 3.30 (s, $W_{h/2} = 1.4$ Hz, OMe), 3.08 (d of d, $^3J_{2,3endo} = 5.3$ Hz, $^3J_{2,3exo} = 10.4$ Hz, H2), 2.48 (m, H1), 2.30 (m, H5), 2.03* ($H8_{syn}$), 1.99# (m, $H3_{endo}$), 1.79# (d of d of t, $^2J_{3exo,3endo} = 13.3$ Hz, $^3J_{3exo,2} = {}^2J_{3exo,4endo} = 9.8$ Hz, $^3J_{3exo,4exo} = 6.0$ Hz, $H3_{exo}$), 1.72* ($H9_{syn}$), 1.61# (m, $H4_{exo}$), 1.58* ($H9_{anti}$), 1.57* ($H8_{anti}$), 1.50# (m, $H4_{endo}$); ^{13}C NMR ($CDCl_3$) δ_C 138.5 (C6), 131.1 (C7), 79.5 (C2), 56.0 (OMe), 36.1 (C1), 30.6 (C3), 30.5 (C5), 30.3 (C4), 24.3 (C9), 20.3 (C8); MS ($C_{10}H_{16}O$) $M^{\bullet+}$ requires 152.1201, found 152.1203.

Reaction of *exo*-Tricyclo[3.2.2.$0^{2,4}$]non-6-ene (1) with a Catalytic Amount of PTSA in Methanol-d_1. A solution of **1** (424 mg, 3.53 mmol) and PTSA (50 mg, 0.26 mmol, 0.07 mol equiv) in 95% methanol-d_1 (3 mL) was heated for 10 days at 80 °C in a sealed tube, after which time GLC analysis showed the reaction to be complete. The reaction mixture was poured into water (7 mL) and extracted with ether (16 mL). The ether extract was washed with a saturated brine solution and dried over $MgSO_4$, and the solvent was removed under reduced pressure to give a brown oil (292 mg, ca. 54% recovery). GLC analysis of the resulting oil showed three peaks, 71%, 16%, and 13%. The major peak was collected by preparative GLC and shown (^{13}C and ^{2}H NMR) to contain two products: 4-*exo*-deuterio-2-*exo*-methoxybicyclo[3.2.2]non-6-ene (**4**) (40%) and 4-*endo*-deuterio-2-*exo*-methoxybicyclo[3.2.2]non-6-ene (**5**) (31%). Two other products (16% and 13%) were not identified. The ratio of **4** and **5** was determined from integration of the ^{2}H NMR spectrum (ratio 1.3:1.0). **4** and **5**: colorless oil; (the following assignments were made for both molecules)

(19) ^{2}H NMR spectra were run unlocked with CCl_4 as the solvent.

(20) The *exo* and *endo* deuterium at C4 can be confidently assigned since the chemical shifts of the C4 protons are known. The possibility of some deuterium scrambling (Fry, J. L.; Karabatos, G. J. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley and Sons: New York, 1970; Vol. 2, Chapter 14) from C4 to C3 cannot be completely eliminated. Deuterium at C3 would usually be detected from the ^{13}C NMR spectrum by spitting of the carbon peak at C3. The similarity of the chemical shifts of C3 and C4 do not allow a minor component with deuterium at C3 to be detected. There is limited charge development at the carbon where nucleophilic addition takes place and proton/deuterium scrambling is considered unlikely.

(21) For *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene, 15% of the reaction was found to occur at the double bond.[1,3]

(22) Rhodes, Y. E.; Schueler, P. E.; DiFate, V. G. *Tetrahedron Lett.* **1970**, 2073.

(23) Schueler, P. E.; Rhodes, Y. E. *J. Org. Chem.* **1974**, *39*, 2063.

^{1}H NMR (CCl_4) δ_H 6.21 (t, $^3J_{6,5} = {}^3J_{6,7} = 8.3$ Hz, H6), 5.97 (t, $^3J_{7,1} = {}^3J_{7,6} = 8.5$ Hz, H7), 3.20 (s, $W_{h/2} = 1.2$ Hz, OMe), 2.98 (d of d, $^3J_{2,3endo} = 10.3$ Hz, $^3J_{2,3exo} = 5.4$ Hz, H2), 2.42 (m, H1), 2.28 (m, H5), 1.97* ($H8_{syn}$), 1.90* ($H3_{endo}$), 1.74* ($H3_{exo}$), 1.52–1.62 (m, $H8_{anti}$, $H9_{anti}$, $H9_{syn}$); (the following proton chemical shifts were assigned to the indicated compounds) **4**, 1.46 ppm ($H4_{endo}$) and **5**, 1.59 ppm ($H4_{exo}$); ^{13}C NMR (CCl_4) δ_C 137.9 (C6), 131.0_8 and 131.1_1 (C7), 78.8 (C2), 55.4 (OMe), 35.9_2 (C1), 30.3_0, 30.2_8, 30.1_8, 30.0_6, 24.4 (C9), 20.1 and 20.0 (C8); ^{2}H NMR (CCl_4) δ_D **4**, 1.80 ($D4_{exo}$), and **5**, 1.65 ($D4_{endo}$); MS ($C_{10}H_{15}{}^2H_1O$) $M^{\bullet+}$ requires 153.1264, found 153.1264; deuterium incorporation 10% D_0, 90% D_1; (the following assignments were made using $CDCl_3$ as the NMR solvent) ^{1}H NMR ($CDCl_3$) δ_H 6.29 (m, H6), 6.04 (m, H7), 3.30 (s, OMe), 3.10 (m, H2), 2.49 (m, H1), 2.30 (m, H5), ^{13}C NMR ($CDCl_3$) δ_C 138.5 (C6), 131.1 (C7), 79.5 (C2), 56.0 (OMe), 36.1 (C1), 30.6, 30.5, 30.3, 24.3 (C9), 20.3 and 20.2 (C1).

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Supporting Information Available: ^{1}H, ^{2}H, and ^{13}C NMR spectra of **2** and deuterated **2** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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