Bromination of *exo*-Tricyclo[3.2.2.0^{2,4}]non-6-ene

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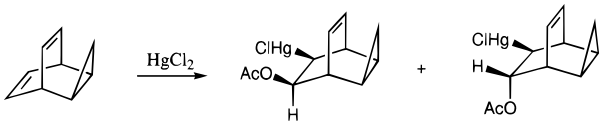
In carbon tetrachloride reaction of **1** with bromine occurs at the double bond and is favored from the less hindered face, *anti* to the cyclopropane ring, to give **2** and **3** (2:1) over reaction from the *syn* face or at the corner of the cyclopropane to give **5**. In the solvent methanol, corner attack of bromine at the cycloproane to give **30**, **16**, **17**, and **37** competes with reaction at the double bond *anti* to the cyclopropane to give **18**, **19**, and **2**.

The reactivity of cyclopropanes, which is generally considered to parallel that of alkenes more closely than that of other cyclic hydrocarbons, allows their use as synthetic imtermediates.[1] Reaction with electrophiles initiates 1,3-difunctionalization, and ring opening may lead to ring expansion. If the full potential of cyclopropanes in organic synthesis is to be realized, then the factors which affect regiochemistry and stereospecificity of the ring-opening process need to be understood.

We have previously reported experimental studies to elucidate the trajectory of electrophilic attack ($H^+/D^+/Hg(OAc)_2$[2] /Br_2[3]) on cyclopropanes contained within tricyclo[3.2.1.0^{2,4}]octane and -oct-6-ene carbon skeletons.[4] Inclusion of the cyclopropane into bridged structures of this type allows definitive determination of the trajectory of electrophilic attack on the cyclopropane ring and, in the case of compounds containing both a cyclopropane ring and a double bond, allows the competition for electrophilic attack, between the double bond and the cyclopropane ring, to be determined. The results of these studies show that electrophilic addition generally takes place at the cyclopropane ring. Reaction generally occurs with inversion of configuration at the site of electrophilic attack and cleavage of the most substituted cyclopropyl (C2C4) bond results. For *endo*- and *exo*-tricyclo[3.2.1.0^{2,4}]-oct-6-ene reaction with H^+/D^+ occurs with rupture of the cyclopropane ring in preference to reaction at the double bond. In contrast, for *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene, bromine and $Hg(OAc)_2$ react regiospecifically at the double bond. The regiochemistry and stereochemistry of the reactions depends on the structure of the starting compound. Acid-catalyzed addition to *exo*-tricyclo[3.2.2.0^{2,4}]-non-6-ene occurs by rupture of the internal carbon−carbon bond of the cyclopropane with both retention and inversion at the site of electrophilic attack (1.3:1)[5] in contrast to the reaction of *exo*-tricyclo[3.2.1.0^{2,4}]octane, where only inversion at the site of electrophilic attack is observed.[2b]

To extend the scope of these studies and to test the generality of these results, experimental studies concerning the addition of bromine to *exo*-tricyclo[3.2.2.0^{2,4}]non-6-ene are now reported. A number of reactions involving electrophilic addition to compounds containing a tricyclo[3.2.2.0^{2,4}]non-6-ene carbon skeleton have been reported and both "Markovnikov"[6] and "*anti*-Markovnikov" products have been reported.[4,7] The presence of substituents in the compounds complicates any analysis of orbital effects on the trajectory of electrophilic addition to the cyclopropane ring.[6] The use of unsubstituted and/or symmetrical systems allows the effect of orbital/electronic and steric factors on the course of reaction to be more easily and unambiguously established. The studies of *exo*-tricyclo[3.2.2.0^{2,4}]non-6-ene were directed toward determining if the C9 tricyclic hydrocarbon, where the cyclopropane is in a slightly different orientation with respect to the alkene, shows different stereochemistry and regiochemistry of bromine addition from those observed for the analogous C8 hydrocarbon tricyclo[3.2.1.0^{2,4}]oct-6-ene.[8]

The reaction of bromine (0.9 mol equiv)[9] with *exo*-tricyclo[3.2.2.0^{2,4}]non-6-ene (**1**) in CCl_4 proceeded essentially instantaneously at room temperature to give 5-*endo*-9-*syn*-dibromo-*endo*-tricyclo[4.2.1.0^{2,4}]nonane (**2**) (38%), 5-*endo*-9-*syn*-dibromobicyclo[4.2.1]non-2-ene (**3**)



2.3 : 1.0

This has been attributed to the increased size of the orbital coefficients of C6 and C7 in tricyclo[3.2.2.0^{2,4}]nona-6,8-diene due to the large through-space interaction with the es orbital of the cyclopropyl ring ($\langle\pi/\sigma s\rangle = 0.061$) which compares with 0.052 and 0.012 for hydrocarbons *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene and *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene, respectively. Gleiter, R.; Bohm, M. C.; de Meijere, A.; Pruess, T. *J. Org. Chem.* **1983**, *48*, 796. Srinivasan, R.; Ors, J. A.; Brown, K. H.; Baum, T.; White, L. S.; Rossi, A. R. *J. Am. Chem. Soc.* **1980**, *102*, 5297. This results in better overlap of the hydrocarbon π orbitals with the Hg^{2+} LUMO. A similar explanation has been proposed for the reactivity of *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene. In the case of *endo*-tricyclo[3.2.1.0^{2,4}]-oct-6-ene the smaller π orbital coefficients in the HOMO of the double bond result in exclusive cyclopropyl ring opening.

(9) Less than 1 mol equiv of bromine was used in order to avoid the risk of forming tetrabromo products.

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(2) (a) Coxon, J. M.; Steel, P. J.; Whittington, B. I.; Battiste, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 2988. (b) Coxon, J. M.; Steel, P. J.; Whittington, B. I. *J. Org. Chem.* **1989**, *54*, 1383. (c) Coxon, J. M.; Steel, P. J.; Whittington, B. I. *J. Org. Chem.* **1989**, *54*, 3702. (d) Coxon, J. M.; Steel, P. J.; Whittington, B. I. *J. Org. Chem.* **1990**, *55*, 4136.(e) Burritt, A.; Coxon, J. M.; Maclagan, R. G. A. R. *Tetrahedron* **1995**, *51*, 8057.

(3) (a) Burritt, A.; Coxon, J. M.; Steel, P. J.; Whittington, B. I. *J. Org. Chem.* **1995**, *60*, 2812. (b) Coxon, J. M.; Steel, P. J.; Burritt, A.; Whittington, B. I. *Tetrahedron* **1995**, *51*, 8057. (c) Burritt, A.; Coxon, J. M.; Steel, P. J. *J. Org. Chem.* **1995**, *60*, 7670.

(4) (a) Burritt, A.; Coxon, J. M.; Steel, P. J. In *Trends in Organic Chemistry*; Research Trends, Council of Scientific Research Integration: India, 1993; Vol. 4, pp 517−534.

(5) Burritt, A.; Coxon, J. M.; Steel, P. J. *J. Org. Chem.* **1995,** in **B**.

(6) Zimmerman, M. P.; Li. H. T.; Duax, W. L.; Weeks, C. M.; Djerassi, C. *J. Am. Chem. Soc.* **1984**, *106*, 5602.

(7) (a) Hendrickson, J. B.; Boeckman, R. K., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 3269. (b) McManus, L. D.; Rogers, N. A. J. *Tetrahedron Lett.* **1969**, 4735. (c) Müller, E. *Chem. Ber.* **1976**, *109*, 3793.

(8) Reaction of tricyclo[3.2.2.0^{2,4}]nona-6,8-diene with mercuric acetate[6] gave predominantly mercuric ion addition to the C6C7 double bond, similar to that found for the reaction of $Hg(OAc)_2$ with *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene in preference to addition to the cyclopropane ring as was observed for *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene.[2c,4]

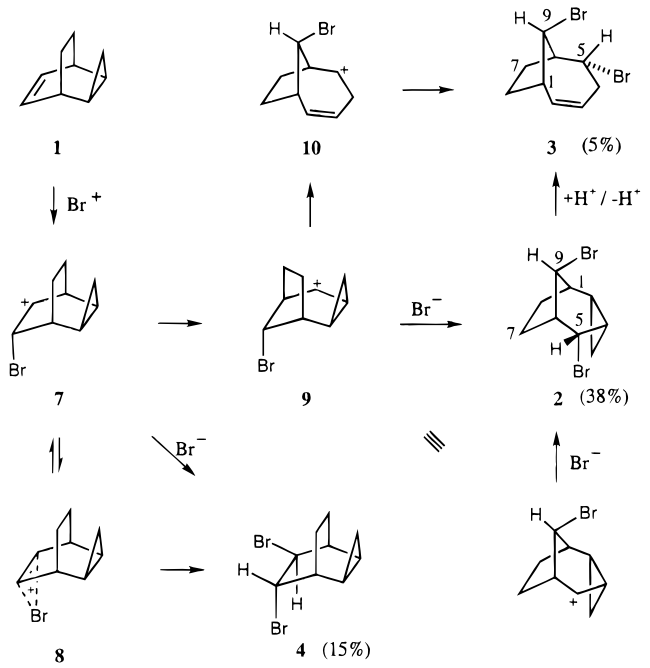


Figure 1. Reaction of **1** with bromine in CCl_4—attack of Br^+ *anti* to the cyclopropane.

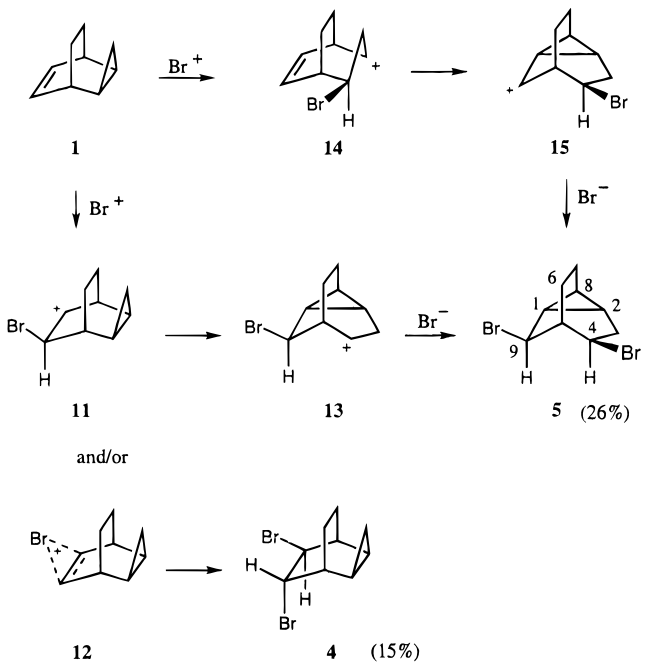


Figure 2. Reaction of **1** with bromine in CCl_4—attack of Br^+ *syn* to the cyclopropane.

(ca. 5%) (the only isolated compound of several minor products), 6-*exo*-7-*endo*-dibromo-*exo*-tricyclo[3.2.2.0^{2,4}]-nonane (**4**) (15%) (Figure 1), and 4-*endo*-9-*anti*-dibromo-tricyclo[3.3.1.0^{2,8}]nonane (**5**) (26%) (Figure 2).

The identities of structures **2**−**5** were established by NMR methods.[10] For **2** the structure was confirmed by single-crystal X-ray analysis. The major product **2** is considered to arise from addition of Br^+ to the less hindered face of the alkene, *anti* to the cyclopropane, to form the open carbocation **7** or the bromonium ion **8**[11] and rearrangement to the cyclopropylcarbinyl cation **9**. Capture of this cation *anti* to the C9Br gives **2**. The stereochemistry of nucleophilic attack reflects either the orientation of the vacant p orbital at C5 and/or electronic or steric interaction of the incoming nucleophile with the C9 bromine substituent.[12]

Formation of **3** is considered to result from subsequent opening of the cyclopropane ring in **9** to give cation **10** and nucleophilic addition from the less hindered face of the cation (Figure 1). Dibromide **4** arises from *trans* addition of bromine to the alkene group of **1**. Since the electrophile and nucleophile cannot be distinguished, the facial selectivity of the electrophile and nucleophile cannot be determined except that the addition is *trans*. The formation of **5** can occur by either addition of Br^+ to the alkene moiety *syn* to the cyclopropane, formation of the classical cation **11,** or the bromonium ion **12**, followed by rearrangement to cation **13** and capture by bromide. An alternate pathway involves electrophilic attack at the cyclopropane ring to give **14**, rearrangement to cyclopropylcarbinyl cation **15**, and capture by bromide. The former pathway might be considered the more likely as bromine addition to a double bond is generally faster than to cyclopropanes[3c] (Figure 2). However, when the reaction is conducted in methanol (see below) formation of **16** and **17** is only consistent with electrophilic attack at the cyclopropane. This suggests that **5** is formed not by reaction at the alkene, but at the cyclopropane. For nucleophilic attack at **9** and **13** or **15**, addition from the observed face to give **2** and **5** must at least be the predominant trajectory due to the large proportion of these products formed. For these cations and **10**, nucleophilic addition to the opposite face of the p orbital to that required for formation of **2**, **3**, and **5**, respectively, cannot be excluded since some 15% of the reaction mixture is unaccounted for.

In order to differentiate electrophile from nucleophile, reaction of **1** with bromine (0.8 mol equiv) in methanol was studied. Reaction was rapid at room temperature. Analysis of a ^{1}H NMR spectrum of the crude reaction mixture showed the presence of three major products and several minor products: 9-*syn*-bromo-5-*endo*-methoxy-*endo*-tricyclo[4.2.1.0^{2,4}]nonane (**18**, 34%), and 5-*endo*-9-*syn*-dibromo-*endo*-tricyclo[4.2.1.0^{2,4}]nonane (**2,** 3%), 9-*syn*-bromo-5-*endo*-methoxybicyclo[4.2.1]non-2-ene (**19**, 3%) (Figure 3) 4-*endo*-9-*anti*-dimethoxytricyclo[3.3.1.0^{2,8}]nonane (**20**, 24%), 4-*endo*-9-*syn*-dimethoxy-tricyclo[3.3.1.0^{2,8}]nonane (**21**, 14%) (Figure 4), 4-*endo*-bromo-9-*anti*-methoxytricyclo-[3.3.1.0^{2,8}]nonane (**16**, 5%), and 4-*endo*-bromo-9-*syn*-methoxytricyclo[3.3.1.0^{2,8}]nonane (**17**, 5%) (Figure 5).

The identity of **18**−**21** follows from NMR studies.[10] Further support for the structure assignment of **19** and for the stereochemistry of C5 was gained from comparison of the coupling constants observed for this structure with those of compound **3** and from comparison of the observed coupling constants with those calculated[10] for the geometries resulting from molecular mechanics conformational searches of **19** and its isomer 9-*syn*-bromo-5-*exo*-methoxybicyclo[4.2.1]non-2-ene (**22**). The average deviation of the calculated coupling constants from those

(10) See supporting information.

(11) For the bicyclo[2.2.1.0^{2,4}]oct-6-ene the *exo* nonclassical bromonium ion formed by bromine attack at the double bond has been calculated to be higher in energy than the corresponding classical ion due to the interaction of the bromine in the nonclassical ion with the *syn* C8 hydrogen.[3b] This interaction does not exist for the corresponding nonclassical ion formed from bromine attack at **1**.

(12) This has also been observed in the reactions of other tricyclo-[4.2.1.0^{2,4}]nonane derivatives. Kirmse, W.; Wahl, K.-H. *Chem. Ber.* **1974**, *107*, 2768.

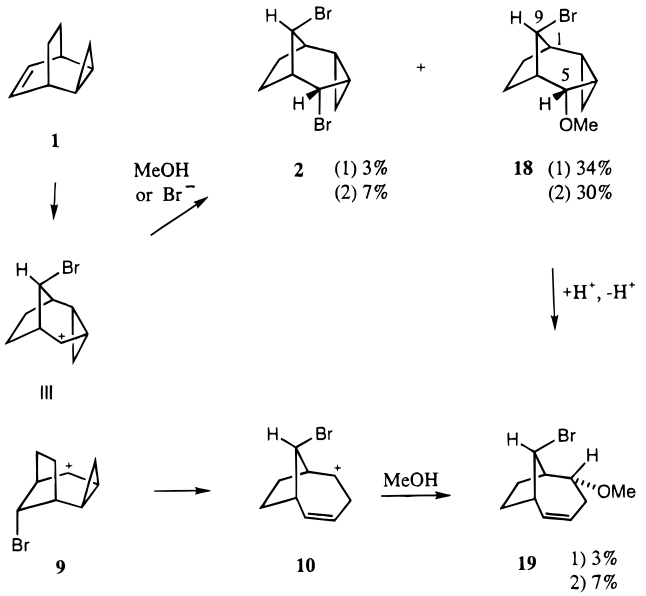


Figure 3. Reaction of Br^+ with **1***anti* to the cyclopropane: (1) in methanol at room temperature and (2) 0 °C.

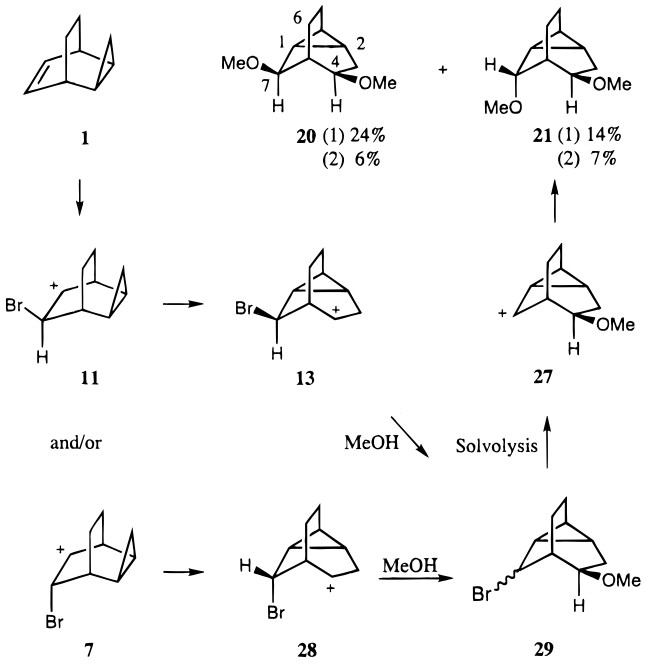


Figure 4. Reaction of Br^+ at the alkene *syn* or *anti* to the cyclopropane in methanol at (1) room temperature and (2) 0 °C.

observed for **19** is 1.0 Hz, compared with an average deviation of 2.2 Hz for **22**. Of particular note is the coupling constant of H5 to H4*endo* which shows a 0.5 Hz deviation between the observed and calculated values for **19**, while for **22** the difference would be 8.1 Hz.

Additional support for the structure assignments of **20** and **21** came from comparison of the coupling constants observed with those calculated[10] for the four 4,9-dimethoxytricyclo[3.3.1.$0^{2,8}$]nonane isomers **20**, **21**, **23**, and **24**. The conformational space for each compound was searched using Monte Carlo molecular mechanics techniques. In each case the smallest average error in coupling constants is obtained for the assigned structure with respect to the calculated values (0.5 Hz average error between the calculated and observed coupling

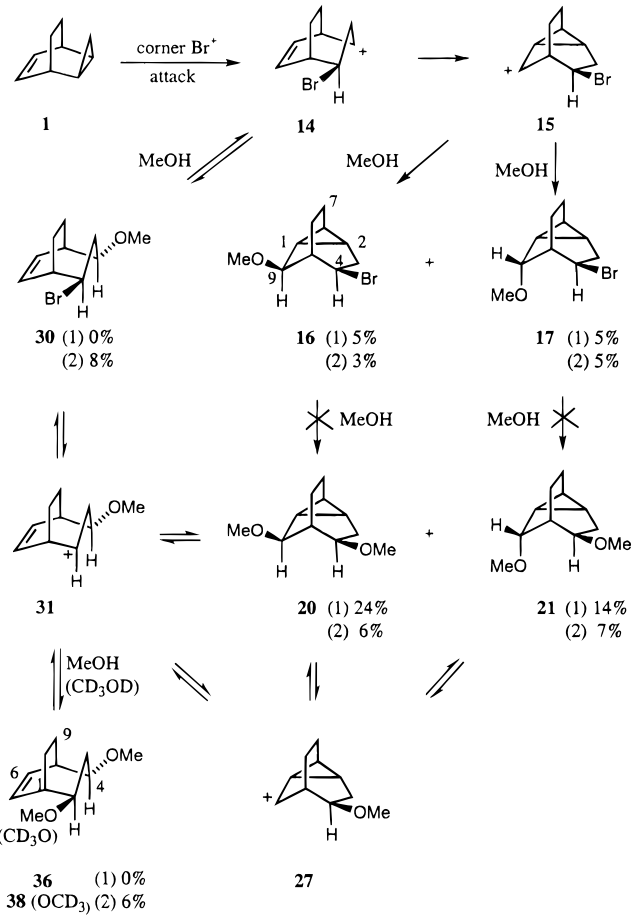
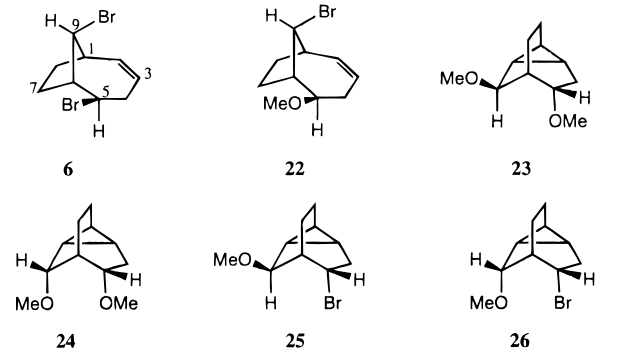


Figure 5. Alternative mechanism for formation of **20, 21, 16, 17**, **30**, and **36** involving corner attack of Br^+.

constants for **21** and a 0.4 Hz average error for **20**). The calculated coupling constants in conjunction with the NOE data serve to exclude the other possible structures.[13]



The identity of **16** and **17** were determined from NMR studies and supported[10] from comparison of the observed coupling constants for this molecule with those calculated for the four possible isomeric 4-bromo-9-methoxytricyclo-

(13) For compound **21** the difference in the calculated and observed coupling constant for $^3J_{3endo,4}$ may be due to the calculation method, which was derived empirically, without a sufficiently high representative number of bicyclic and tricyclic molecules. The NMR program implements an empirical generalization of the Karplus equation developed by Haasnoot et al. (Haasnoot, C. A. G.; De Leeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2783) for calculation C(sp3)−C(sp3)−H coupling constants and Garbisch, Jr., E. W. for calculation of H−C(sp2)−C(sp3)−H coupling constants (*J. Am. Chem. Soc.* **1964**, *86*, 5561). The errors found in calculation of the three bond coupling constants are consistent with those reported in the above references for other systems of this type.

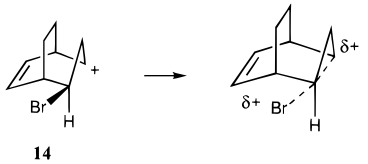
[3.3.1.0^{2,8}]nonane structures **16**, **17**, **25**, and **26**. The conformational space of each isomer was searched using Monte Carlo molecular mechanics techniques and the Boltzmann averaged coupling constants for the conformations of each isomer found within a 12.5 kJ mol^{-1} energy window calculated. For **16** and **17** the calculated coupling constants are in best agreement with the observed values for the structures assigned, with average errors between the calculated and observed coupling constants of 0.6 and 0.7 Hz, respectively.

Formation of **18**, **2**, and **19** (Figure 3) accounts for 37% at room temperature (44% at 0 °C), of the reaction and arises by a mechanism similar to those outlined for the formation of **2** and **3** in the absence of methanol (Figure 1). For these products the reaction is initiated by attack of bromine at the alkene and specifically from the less hindered face *anti* to the cyclopropane. The formation of **18**, in this reaction, where the electrophile and nucleophile are differentiated, confirms that formation of **2** is initiated by attack of a bromine electrophile at the face of the alkene *anti* to the cyclopropane (Figure 1). In methanol, a small amount of **2** (3%) is observed where bromide competes with methanol as nucleophile.

The other two major products **20** (analogous to **5** formed in the absence of methanol) and **21** did not contain a bromine substituent and have arisen from solvolysis of a primary product(s) of reaction. A preference for formation of the *syn* dimethoxy adduct **20** (*syn*:*anti*: ratio 1.7:1) is observed. The formation of **20** and **21** is consistent with either the intermediacy of cation **27** as shown in Figure 4, where reaction is initiated at the alkene, or via a mechanism that involves bromine attack, not at the alkene, but at the cyclopropane (Figure 5). The former sequence involves attack of bromine at the alkene either *syn* or *anti* in **1** to give cations **7** or **11** followed by rupture of the cyclopropane, bridging from C2C7 (or C4C6) with cyclopropyl carbinyl cation formation (**28** and **13**), followed by methanol attack to give **29** and methanolysis via **27** leads to **20** and **21** (Figure 4). In this route any information about the stereochemistry of the initial electrophilic attack by bromine at the alkene is lost in the final solvolysis to **27**.

There are two alternative mechanisms for the formation of **20** and **21** which both involve bromine attack, not at the alkene, but at the corner of the cyclopropane of **1** (Figure 5) to give cation cation **14**.[14] In the first of these mechanisms, cation **14** is captured by methanol to give **30** which on subsequent solvolysis via **31** would give **20** and **21**. In a separate experiment, involving reaction of **1** with bromine in methanol at 0 °C, **30** was isolated from the reaction. Competing with solvent capture of cation **14** is rearrangement to cation **15** and formation of **16** and **17**. The second route to **20** and **21** involves solvolysis of **16** and **17**. A separate experiment showed that **17** and **16** are equally stable to heating in methanol-d_4 and hence the intermediacy of **16** and **17** in the formation of **20** and **21** in the reaction with bromine in methanol at 0 °C or room temperature can be excluded.

(14) This cation may be bridged: see ref 2.



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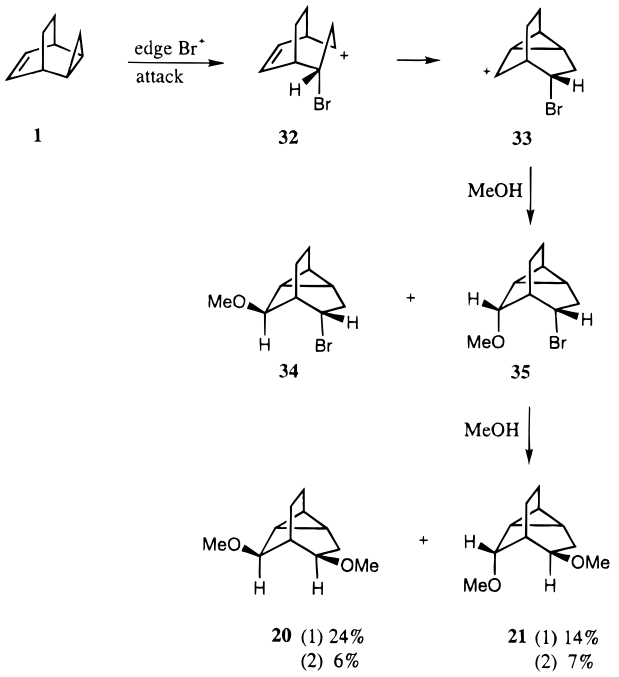

Figure 6. Alternative mechanism for formation of **20** and **21** involving edge attack of Br^+.

A further mechanism to give **20** and **21** involves edge attack of bromine at the cyclopropane ring (Figure 6) followed by rearrangement and nucleophilic capture of cations **32** and **33**, respectively, to give rise to **34** and **35** (which were not isolated) followed by solvolysis. No products with an orientation of bromine at C4 that require edge bromine addition have been isolated and hence this pathway seems unlikely.[15] Furthermore solvolysis of the bromine substituent of C4 in **16**/**17** and **34**/**35** which would give homocyclopropylcarbinyl cations would be expected to be a even less facile process than solvolysis of the C9 bromine substituent of **29** to a cyclopropylcarbinyl cation intermediate (Figure 4).

In an attempt to stop the solvolysis of the primary bromo products, the reaction of **1** with bromine in methanol was repeated at 0 °C. The reaction gave, in addition to **18** (30%), **2** (7%), **19** (7%) (Figure 3), **20** (6%), **21** (7%), (Figure 4), **16** (3%), **17** (5%) (Figure 5) which were observed in the reaction at room temperature, the following three products: 2-*exo*-bromo-4-*exo*-methoxybicyclo[3.2.2]non-6-ene (**30**, 8%), 2-*exo*-4-*exo*-dimethoxybicyclo[3.2.2]non-6-ene (**36**, 6%) and 2-*exo*-bromo-9-*syn*-methoxybicyclo[3.2.2]non-6-ene (**37**, 3%) (Figure 7). The identity of **30**, **36**, and **37** were determined from NMR studies.

When the reaction was performed at 0 °C the yields of **20** and **21** were reduced.[16] Compounds **29**, which could be precursors to **20** and **21**, were not isolated. Three new products **30**, **36**, and **37** were isolated. The formation of **30** can only occur by corner attack of bromide at C2 with inversion followed by capture of the cation by methanol. Solvolysis of **30** to the homoallylic cation **31** and capture with retention of configuration would afford **36** along with

(15) This is supported by the results obtained from bromination of *endo*- and *exo*-tricyclo[3.2.1.0^{2,4}]octane and 2-methyl-*endo*-tricyclo[3.2.1.0^{2,4}]octane which occurred via corner attack.[3] However, the effect of a double bond, in this geometric relationship to the cyclopropane ring, on edge bromination has not been determined.

(16) This reaction proved to be very sensitive to the reaction conditions and was not always reproducible.

20 and **21** (Figure 5). The formation of **36** could also occur by methanolysis of **20** and/or **21** to give cation **27** followed by ring opening to give **31** and reaction with methanol. The dimethoxy compounds **20** and **21** are in fact unstable under reflux conditions in methanol for 1 h. When a mixture of **18** and **19** was heated in methanol-d_4 for 1 h, the ^{1}H NMR of the resulting products showed the complete disappearance of **20** and approximately 60% loss of **21**. Compounds **18**, **17,** and **19** (Figure 3) were stable to reflux in methanol-d_4. This demonstrates that formation of **20** and **21** does not proceed by methanolysis of **16** and **17**.[17]

The main product resulting from reflux of **18** and **19** with methanol-d_4 was 4-*exo*-methoxy-2-*exo*-(trideuteriomethoxy)bicyclo[3.2.2]non-6-ene (**38)** identified from analysis of the ^{1}H and ^{13}C NMR spectra of the reaction mixture and comparison with authentic undeuterated **36**. The assignment was supported by GCMS results which showed the molecule to contain three deuterium atoms. From an analysis of ^{1}H and ^{13}C NMR spectra some correlation was observed between the formation of **38** and the disappearance of **20** and **21**. The presence of only three deuterium atoms in **38** precludes the possibility of acid-induced ring opening in the formation of **36** as this would be expected to result in incorporation of four deuterium atoms into the product. Another route to **36** from **20** and **21** could involve addition of methanol to the cyclopropane followed by selective elimination.

To check the stability of the products in methanol at room temperature and to determine whether product solvolysis was occurring on workup, the reaction was performed in methanol-d_4 at ca. −25 °C in an NMR tube and then rapidly inserted into the NMR spectrometers probe which was precooled to −20 °C. A ^{1}H NMR spectrum recorded after ca. 5 min showed, by the absence of signals due to **1**, that the reaction was complete.[18] The sample was gradually warmed to room temperature in the probe, and the reaction mixture monitored by ^{1}H NMR. No product degradation or change in product ratios was evident on warming. The solvent was removed and half of the residue redissolved in methanol-d_4 and a ^{1}H NMR spectrum obtained demonstrated that the products of reaction did not decompose on workup. The second half of the crude reaction mixture was taken up with $CDCl_3$ and the products identified from comparison with the data already determined. In this case the deuterated analogues of compounds **18**, **20**, and **21** were the major products and must be formed from a facile solvolysis reaction that takes place even at −20 °C. These products are not artifacts of the workup procedure.

The most direct pathway for the formation of **30** appears to be via corner addition of the bromine electrophile to **1** followed by capture of the resulting cation **14** by methanol before rearrangement occurs. However, solvolysis of **20** or **21** via **27** followed by nucleophilic capture of cation **31** by bromine or direct nucleophilic attack on the cyclopropane ring cannot be ruled out. A possible pathway for the formation of **37** is via a 1,3-hydride shift in cation **14** to give **39** which then undergoes nucleophilic attack to form **37** (Figure 7).

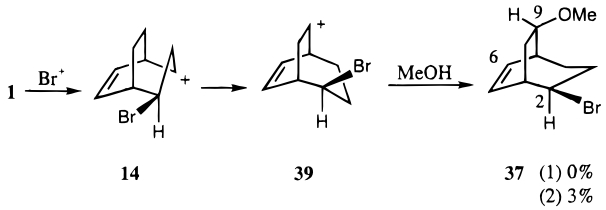

Figure 7. Mechanism for formation of **37**.

In the bromination of **1**, in CCl_4, electrophilic addition to give **2** and **3** is favored at the double bond in preference to reaction at the more hindered face *syn* to the cyclopropane or at the corner of the cyclopropane to give **5**. In the solvent methanol, products **30**, **16**, **17**, and **37** are considered to arise from bromination of the cyclopropane ring (total ca. 20%) and competing with corner attack is reaction at the alkene *anti* to the cyclopropane to give **18**, **19**, and **2**. The stereochemistry of the reaction of electrophile and nucleophile in the formation of dibromide **4** cannot be determined and formation of **20** and **21** could be formed by either or both of two mechanisms. The chemistry of **1**, where reaction of bromine occurs both at the alkene and at the cyclopropane, differs from that of *exo*- and *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene[3b] and *endo*-2-methyltricyclo[3.2.1.0^{2,4}]oct-6-ene[3c] where only products of reaction of bromine at the alkene are observed.

Experimental Section

NMR spectra were recorded with a 5 mm probe and operating at 300 MHz 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. Difference NOE spectra were obtained in arrayed experiments with the decoupler offset 10 000 Hz and then cycled with low power over the multiplet peaks of the desired proton for irradiation, a procedure based on that of Kinns and Sanders.[19] Carbon-detected heteronuclear proton−carbon-correlated (HETCOR) spectra were recorded using a pulse sequence which ensures full ^{1}H−^{1}H decoupling.[20] All other experiments were recorded using standard pulse sequences and parameters. Proton chemical shifts marked with a superscript asterisk were estimated from NOE or two-dimensional NMR experiments (COSY, DQCOSY, HETCOR, or HMQC experiments). Infrared spectra were recorded on a Perkin-Elmer 1600 Series FT-IR spectrometer. Mass spectra were recorded by GCMS directly coupled to a GLC fitted with a Restex R_{tx}1 30 m × 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 per minute up to 260 °C) to ensure that the sample and all impurities passed through the column to the MS instrument. In some cases molecular ion peaks were not observed in the high-resolution mass spectra (HRMS) but were identified in the low-resolution spectra (LRMS), in these cases the LRMS and HRMS spectra are shown along with a number of fragment ion peaks which were observed. Analytical and preparative GLC was carried out using either a 1.5% OV-17, 1.25% QF-1 Chromosorb W packed column of 5 mm external diameter and 3.0 m length or a 1.5% OV-17, 1.95% QF-1 Chromosorb W packed column of 10 mm external diameter and 2.5 m length. TLC mesh column chromatography was performed on Merck 60PF$_{254+366}$ grade silica gel. Radial chromatography was performed using Merck grade 60PF$_{254}$ silica gel or polyethylene glycol (PEG, molecular weight 6000 g mol^{-1})-coated silica plates. Melting points were determined on an electrothermal melting point apparatus and

(17) This could not be confirmed with certainty due to the close proximity of the chemical shifts of the methoxy group of **18** with that of **16**.

(18) The reaction was most likely instantaneous even at −25 °C, although bromine coloration was still evident when the sample was inserted into the NMR probe and after warming to room temperature. A slight excess of bromine was therefore present.

(19) Kinns, M.; Sanders, J. K. M. *J. Magn. Reson.* **1984**, *56*, 518.

(20) Perpick-Dumont, M.; Reynolds, W. F.; Eriquez, R. G. *Magn. Reson. Chem.* **1988**, *26*, 358.

are uncorrected. Elemental analyses were performed at the Department of Chemistry, University of Otago, Dunedin, New Zealand.

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[21] and the identity confirmed by comparison of the ^{1}H NMR spectra with that reported. ***exo*-Tricyclo-[3.2.2.0^{2,4}]non-6-ene (1):** a colorless semisolid; bp 165−168 °C; Lit.[43] bp 162−168 °C; ^{1}H NMR δ_H(CDCl$_3$) 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 δ_C(CDCl$_3$) 137.8 (C6, C7), 29.9 (C1, C5), 23.2 (C8, C9), 21.5 (C2, C4), 14.1 (C3); HRMS C_9H_{12} M$^{\bullet+}$ requires 120.0939, found 120.0934 (37.5%).

Reaction of *exo*-Tricyclo[3.2.2.0^{2,4}]non-6-ene (1) with Bromine in Carbon Tetrachloride. Bromine (366 mg, 2.29 mmol) in CCl_4 (10 mL) was added dropwise to stirred solution of **1** (312 mg, 2.60 mmol, 1.1 mol equiv) in CCl_4 (5 mL) at room temperature. The reaction was stirred for 1 h and then washed with an aqueous solution of sodium metabisulfite and water and dried over $MgSO_4$, and the solvent was removed under reduced pressure to give a yellow oil (560 mg, ca. 87% recovery). GLC analysis showed four products, 5-*endo*-9-*syn*-dibromo-*endo*-tricyclo[4.2.1.0^{2,4}]nonane (**2**, 38%), 4-*endo*-9-*anti*-dibromotricyclo[3.3.1.0^{2,8}]nonane (**5**, 26%), 6-*exo*-7-*endo*-dibromo-*exo*-tricyclo[3.2.2.0^{2,4}]nonane (**4**, 15%), the fourth product (10%) was not identified. A number of minor products were also present, of which 5-*endo*-9-*syn*-dibromo-bicyclo[4.2.1]non-2-ene (**3** ca. 5%) was the only one isolated. Column chromatography (silica gel, 100:1 ratio absorbant to sample, pentane elution) gave pure **4** and **3** but resulted in rearrangement of the two other major products. Radial chromatography on PEG-coated silica plates (pentane elution) gave a crude separation of the major products. Pure **2** was obtained by recrystallization from pentane of an enriched fraction. The third major product **5** was not isolated in high purity, but was assigned from an enriched fraction (ca. 70%) obtained from radial chromatography on a PEG-coated silica plate. **5-*endo*-9-*syn*-Dibromo-*endo*-tricyclo[4.2.1.0^{2,4}]nonane 2:** obtained as colorless crystals; mp 79−80 °C (pentane); ^{1}H NMR δ_H(CDCl$_3$) 5.28 (t, $^3J_{5,4}$ = 7.4 Hz, $^3J_{5,6}$ = 5.7 Hz, H5), 4.03 (t, $^3J_{9,1}$ = $^3J_{9,6}$ = 4.3 Hz, H9), 2.75 (m, H1), 2.47 (m, H6), 1.87 (m, H7*endo*), 1.69* (H2), 1.62* (H7*exo*, H8*exo*), 1.56* (H8*endo*), 1.41 (m, H4), 0.78 (d of t, $^2J_{3exo,3endo}$ = 6.0 Hz, $^3J_{3exo,2}$ = $^3J_{3exo,4}$ = 9.4 Hz, H3*exo*), 0.57 (d of t, $^2J_{3endo,3exo}$ = 5.8 Hz, $^3J_{3endo,2}$ = $^3J_{3endo,4}$ = 5.8 Hz, H3*endo*); ^{13}C NMR δ_C(CDCl$_3$) 59.0 (C5), 56.9 (C9), 44.1 (C6), 37.5 (C1), 25.7 (C8), 24.6 (C2), 23.5 (C7), 15.3 (C4), 12.5 (C3). LRMS $C_9H_{12}{}^{81}Br_2$ M$^{\bullet+}$ requires 282, found 282 (1%); $C_9H_{12}{}^{79}Br^{81}Br$ M$^{\bullet+}$ requires 280, found 280 (3%); $C_9H_{12}{}^{79}Br_2$ M$^{\bullet+}$ requires 278, found 278 (1%); HRMS $C_9H_{12}{}^{79}Br^{81}Br$ M$^{\bullet+}$ requires 279.9287, found 279.9275 (78.0%); $C_9H_{12}{}^{79}Br_2$ M$^{\bullet+}$ requires 277.9307, found 277.9311 (28.9%). **4-*endo*-9-*anti*-Dibromotricyclo[3.3.1.0^{2,8}]nonane (5).** This compound was identified from an enriched mixture (ca. 70%) and a complete assignment was not possible: colorless oil; ^{1}H NMR δ_H(CDCl$_3$) 4.76 (m, $^3J_{9,1}$ = $^3J_{9,5}$ = 3.7 Hz, H9), 4.15 (m, $^3J_{4,3endo}$ = 10.7 Hz, $^3J_{4,3exo}$ = 8.3 Hz, $^3J_{4,5}$ = 2.7 Hz, H4), 2.60 (m, H3*exo*), 2.34 (m, H5), 2.12* (H3*endo*), 1.50 (m, H1), 1.21−1.27 (m, H2, H8); ^{13}C NMR δ_C(CDCl$_3$) 54.0 (C9), 51.0 (C4), 42.1 (C5), 28.2 (C3); the following ^{13}C NMR signals were observed but not assigned: 18.1, 16.1, 15.9, 14.4, 14.0. **6-*exo*-7-*endo*-Dibromo-*exo*-tricyclo[3.2.2.0^{2,4}]nonane (4):** colorless oil; ^{1}H NMR δ_H(CDCl$_3$) 4.53 (m, $^3J_{6,5}$ = 3.5 Hz, $^3J_{6,7}$ = 3.3 Hz, $^4J_{6,9syn}$ = 2.5 Hz, H6), 4.39 (t, $^3J_{7,1}$ = $^3J_{7,6}$ = 3.2 Hz, H7), 2.27* (H5), 2.25* (H1), 1.80 (m, $^4J_{9anti,4}$ = 1.1 Hz, H9*anti*), 1.43−1.54 (m, H8*anti*, H8*syn*), 1.34* (H2), 1.29* (H9*syn*), 1.10 (m, H4), 0.84 (d of t, $^2J_{3exo,3endo}$ = 6.1 Hz, $^3J_{3exo,2}$ = $^3J_{3exo,4}$ = 3.8 Hz, H3*exo*), 0.61 (d of t, $^2J_{3endo,3exo}$ = 5.6 Hz, $^3J_{3endo,2}$ = $^3J_{3endo,4}$ = 8.5 Hz, H3*endo*); ^{13}C NMR δ_C(CDCl$_3$) 61.7 (C6), 61.1 (C7), 35.9 (C5), 35.3 (C1), 24.4 (C8), 17.3 (C9), 14.5 (C4), 9.2 (C2), 6.3 (C3); HRMS $C_9H_{12}{}^{81}Br_2$ M$^{\bullet+}$ requires 281.9267, found 281.9327 (36.6%), $C_9H_{12}{}^{79}Br^{81}Br$ M$^{\bullet+}$ requires 279.9287, found 279.9289 (77.4%), $C_9H_{12}{}^{79}Br_2$ M$^{\bullet+}$ requires 277.9307, found 277.9298 (38.6%). **5-*endo*-9-*syn*-Dibromobicyclo[4.2.1]non-2-ene (3):** colorless oil, ^{1}H NMR δ_H(CDCl$_3$) 5.85 (m, $^3J_{2,1}$ = 8.7 Hz, $^3J_{2,3}$ = 11.2 Hz, $^4J_{2,4endo}$ = 2.8 Hz, H2), 5.59 (m, $^3J_{3,2}$ = 11.2 Hz, $^3J_{3,4exo}$ = 8.6 Hz, $^3J_{3,4endo}$ = 3.4 Hz, H3), 4.74 (m, $^3J_{5,4endo}$ = 11.2 Hz, $^3J_{5,4exo}$ = 5.2 Hz, $^3J_{5,6}$ = 2.0 Hz, H5), 4.25 (t, $^3J_{9,1}$ = $^3J_{9,6}$ = 6.7 Hz, H9), 3.03 (m, $^3J_{6,9}$ = 6.8 Hz, H6), 2.88 (m, H1), 2.80 (m, $^3J_{4endo,2}$ = 3.3 Hz, $^3J_{4endo,3}$ = 3.3 Hz, $^3J_{4endo,5}$ = 11.4 Hz, H4*endo*), 2.70 (m, $^2J_{4exo,4endo}$ = 16.2 Hz, $^3J_{4exo,3}$ = 8.5 Hz, $^3J_{4exo,5}$ = 5.7 Hz, $^3J_{4exo,6}$ = 1.0 Hz, H4*exo*), 2.04−2.20 (m, H7*endo*, H8*exo*), 1.84−1.95 (m, H7*exo*, H8*endo*); ^{13}C NMR δ_C(CDCl$_3$) 137.0 (C2), 127.5 (C3), 56.6 (C9), 53.1 (C6), 52.0 (C5), 42.0 (C1), 36.0 (C4), 29.7 (C8), 23.7 (C7); HRMS $C_9H_{12}{}^{81}Br_2$ M$^{\bullet+}$ requires 281.9267, found 281.9307 (54.4%); $C_9H_{12}{}^{79}Br^{81}Br$ M$^{\bullet+}$ requires 279.9287, found 279.9289 (100.0%); $C_9H_{12}{}^{79}Br_2$ M$^{\bullet+}$ requires 277.9307, found 277.9332 (61.9%).

Reaction of *exo*-Tricyclo[3.2.2.0^{2,4}]non-6-ene (1) with Bromine in Methanol at Room Temperature. A solution of bromine (359 mg, 2.25 mmol) in dry methanol (5 mL) was added dropwise over 10 min to a stirred solution of **1** (329 mg, 2.74 mmol, 1.2 mol equiv) in dry methanol (7 mL) at room temperature. The resulting solution was stirred for 2 h and then poured into an aqueous solution of sodium metabisulfite before being extracted with ether (2 × 15 mL). The ether extracts were combined, washed with a saturated NaCl solution (10 mL), and dried over $MgSO_4$, and the solvent was carefully removed under reduced pressure to give a yellow oil (617 mg). GLC analysis showed the presence of three major products as well as a number of minor products. Due to the overlap of the peaks observed in the GLC (under a variety of conditions) the product ratios were estimated from a ^{1}H NMR spectrum of the reaction mixture. A crude separation of the products was effected by radial chromatography on a PEG-coated silica plate (pentane elution). The products were further purified by preparative GLC. The following compounds were identified: 9-*syn*-bromo-5-*endo*-methoxy-*endo*-tricyclo[4.2.1.0^{2,4}]nonane (**18**, 34%), 4-*endo*-9-*anti*-dimethoxytricyclo[3.3.1.0^{2,8}]nonane (**20**, 24%), 4-*endo*-9-*syn*-dimethoxytricyclo[3.3.1.0^{2,8}]nonane (**21**, 14%), 4-*endo*-bromo-9-*anti*-methoxytricyclo[3.3.1.0^{2,8}]nonane (**16**, 5%), 4-*endo*-bromo-9-*syn*-methoxytricyclo[3.3.1.0^{2,8}]nonane (**17**, 5%), 9-*syn*-bromo-5-*endo*-methoxybicyclo[4.2.1]non-2-ene (**19**, 3%), and 5-*endo*-9-*syn*-dibromo-*endo*-tricyclo[4.2.1.0^{2,4}]nonane (**2**, 3%). A number of other minor products were also present but were not identified. 5-*endo*-9-*syn*-Dibromo-*endo*-tricyclo[4.2.1.0^{2,4}]-nonane (**2**) was identified by comparison with the ^{1}H NMR data reported above. **9-*syn*-Bromo-5-*endo*-methoxy-*endo*-tricyclo[4.2.1.0^{2,4}]nonane (18):** colorless oil; ^{1}H NMR δ_H-(CDCl$_3$) 4.12 (t, $^3J_{5,4}$ = $^3J_{5,6}$ = 6.7 Hz, H5), 4.04 (t, $^3J_{9,1}$ = $^3J_{9,6}$ = 4.9 Hz, H9), 3.40 (s, $W_{h/2}$ = 1.0 Hz, OMe), 2.63 (m, $^3J_{1,2}$ = 6.9 Hz, $^3J_{1,8}$ = $^3J_{1,9}$ = 4.3 Hz, H1), 2.44 (m, $^3J_{6,5}$ = $^3J_{6,7}$ = $^3J_{6,9}$ = 6.3 Hz, H6), 1.57* (H7*endo*), 1.53* (H8*endo*), 1.42* (H2), 1.40* (H8*exo*), 1.34* (H7*exo*), 1.16 (m, $^3J_{4,3endo}$ = 5.6 Hz, $^3J_{4,3exo}$ = 8.9 Hz, $^3J_{4,5}$ = 7.2 Hz, H4), 0.58 (d of t, $^2J_{3exo,3endo}$ = 5.4 Hz, $^3J_{3exo,2}$ = $^3J_{3exo,4}$ = 8.8 Hz, H3*exo*), 0.44 (m, $^2J_{3endo,3exo}$ = 5.4Hz, $^3J_{3endo,2}$ = $^3J_{3endo,4}$ = 5.4 Hz, H3*endo*); ^{13}C NMR δ_C(CDCl$_3$) 76.4 (C5), 56.5 (C9), 55.0 (OMe), 39.4 (C6), 37.5 (C1), 25.5 (C8), 19.9 (C7), 19.6 (C2), 10.3 (C4), 7.6 (C3); LRMS $C_{10}H_{15}{}^{81}BrO$ M$^{\bullet+}$ requires 232, found 232 (0.3%); $C_{10}H_{15}{}^{79}BrO$ M$^{\bullet+}$ requires 230, found 230 (0.2%); $C_{10}H_{15}O$ [M − Br]$^{\bullet+}$ requires 151, found 151 (0.5%); HRMS $C_{10}H_{15}O$ [M − Br]$^{\bullet+}$ requires 151.1123, found 151.1130 (39.7%). **4-*endo*-9-*anti*-Dimethoxytricyclo[3.3.1.0^{2,8}]nonane (20):** colorless oil; ^{1}H NMR δ_H(CDCl$_3$) 3.57 (t, $^3J_{9,1}$ = $^3J_{9,5}$ = 3.7 Hz, H9), 3.41 (s, $W_{h/2}$ = 0.7 Hz, OMe), 3.31 (s, $W_{h/2}$ = 0.7 Hz, OMe), 3.23 (d of t, $^3J_{4,3endo}$ = $^3J_{4,3exo}$ = 8.8 Hz, $^3J_{4,5}$ = 3.0 Hz, H4), 2.34 (m, $^2J_{3exo,3endo}$ = 14.2 Hz, $^3J_{3exo,4}$ = 8.8 Hz, H3*exo*), 2.19 (s, $W_{h/2}$ = 10.4 Hz, H5), 2.02 (m, H7*exo*), 1.54* (H7*endo*), 1.53* (H6*endo*), 1.52 (d of d, $^2J_{3endo,3exo}$ = 14.2 Hz, $^3J_{3endo,4}$ = 9.3 Hz, H3*endo*), 1.41 (m, H6*exo*), 1.15 (d of t, $^3J_{1,2}$ = $^3J_{1,8}$ = 8.3 Hz, $^3J_{1,9}$ = 3.4 Hz, H1), 0.97* (H8), 0.96* (H2); ^{13}C NMR δ_C(CDCl$_3$) 78.8 (C4), 76.7 (C9), 55.7 (OMe), 55.6 (OMe), 33.9 (C5), 23.7 (C3), 15.0 (C7), 13.8 (C6), 13.7 (C1), 13.1 (C8), 11.4 (C2); HRMS $C_{11}H_{18}O_2$ M$^{\bullet+}$ requires 182.1307, found 182.1315 (6.8%) $C_{10}H_{14}O$ [M − 32]$^{\bullet+}$ requires 150.1045, found 150.1112 (69.9%). **4-*endo*-9-*syn*-Dimethoxytricyclo[3.3.1.0^{2,8}]nonane**

(21) Rhodes, Y. E.; Schueler, P. E.; DiFate, V. G. *Tetrahedron Lett.* **1970**, 2073. Schueler, P. E.; Rhodes, Y. E. *J. Org. Chem.* **1974**, *39*, 2063.

(21): colorless oil; ^{1}H NMR $\delta_H(CDCl_3)$ 3.75 (t, $^3J_{9,1} = {}^3J_{9,5} =$ 3.4 Hz, H9), 3.55 (m, $^3J_{4,3endo} = 7.7$ Hz, $^3J_{4,3exo} = 9.2$ Hz, $^3J_{4,5} =$ 4.2 Hz, H4), 3.40 (s, $W_{h/2} = 0.6$ Hz, OMe), 3.29 (s, $W_{h/2} = 0.7$ Hz, OMe), 2.48 (m, $^2J_{3exo,3endo} = 14.2$ Hz, $^3J_{3exo,2} = 6.8$ Hz, $^3J_{3exo,4}$ = 9.3 Hz, H3*exo*), 2.21 (m, H5), 1.80* (H7*exo*), 1.78* (H6*endo*), 1.54* (H7*endo*), 1.46 (d of d, $^2J_{3endo,3exo} = 14.2$ Hz, $^3J_{3endo,4} =$ 7.8 Hz, H3*endo*), 1.32 (m, H6*exo*), 1.15 (m, H1), 1.08* (H8), 1.00* (H2); ^{13}C NMR $\delta_C(CDCl_3)$ 78.7 (C9), 73.0 (C4), 55.7 (OMe), 55.6 (OMe), 34.0 (C5), 23.9 (C3), 21.4 (C6), 15.2 (C7), 14.7 (C8), 13.5 (C1), 11.6 (C2); LRMS $C_{11}H_{18}O_2$ $M^{\bullet+}$ requires 182, found 182 (1%); $C_{10}H_{14}O$ $[M - 32]^{\bullet+}$ requires 150, found 150 (100.0%); HRMS $C_{10}H_{14}O$ $[M - 32]^{\bullet+}$ requires 150.1045, found 150.1051 (100.0%). **4-*endo*-Bromo-9-*anti*-methoxytricyclo[3.3.1.0^{2,8}]nonane (16):** colorless oil; ^{1}H NMR $\delta_H(CDCl_3)$ 4.09 (d of t, $^3J_{4,3endo} = 10.4$ Hz, $^3J_{4,3exo} = 8.6$ Hz, $^3J_{4,5} = 2.4$ Hz, H4), 3.64 (t, $^3J_{9,1} = {}^3J_{9,5} = 3.9$ Hz, H9), 3.39 (s, $W_{h/2} = 0.7$ Hz, OMe), 2.55 (m, H3*exo*), 2.28 (s, $W_{h/2} = 9.5$ Hz, H5), 2.09 (d of d, $^2J_{3endo,3exo}$ =14.7 Hz, $^3J_{3endo,4} = 10.6$ Hz, H3*endo*), 2.08* (H7*exo*), 1.65−1.78 (m, H6*endo*, H6*exo*, H7*endo*), 1.20 (m, $^3J_{1,2} = {}^3J_{1,8} = 7.8$ Hz, $^3J_{1,9} = 3.4$ Hz, H1), 1.04* (H2), 1.02* (H8); ^{13}C NMR δ_C-$(CDCl_3)$ 76.9 (C9), 55.8 (OMe), 52.0 (C4), 39.2 (C5), 28.6 (C3), 14.7_6 (C6 or C7), 14.7_2 (C7 or C6), 14.3 (C8), 13.4 (C1), 13.2 (C2); LRMS $C_{10}H_{15}{}^{81}BrO$ $M^{\bullet+}$ requires 232, found 232 (1%), $C_{10}H_{15}{}^{79}BrO$ $M^{\bullet+}$ requires 230, found 230 (1%) $C_9H_{11}{}^{81}Br$ $[M - 32]^{\bullet+}$ requires 200, found 200 (49%) $C_9H_{11}{}^{79}Br$ $[M - 32]^{\bullet+}$ requires 198, found 198 (50%); HRMS $C_9H_{11}{}^{81}Br$ $[M - 32]^{\bullet+}$ requires 200.0025, found 200.0026 (34.2%) $C_9H_{11}{}^{79}Br$ $[M - 32]^{\bullet+}$ requires 198.0045, found 198.0028 (36.7%). **4-*endo*-Bromo-9-*syn*-methoxytricyclo[3.3.1.0^{2,8}]nonane (17):** colorless oil; ^{1}H NMR $\delta_H(CDCl_3)$ 4.56 (d of t, $^3J_{4,3endo} = {}^3J_{4,3exo} =$ 9.3 Hz, $^3J_{4,5} = 2.9$ Hz, $^4J_{4,6exo} = 1.0$ Hz, H4), 3.76 (t, $^3J_{9,1} =$ $^3J_{9,5} = 3.4$ Hz, H9), 3.38 (s, $W_{h/2} = 0.7$ Hz, OMe), 2.70 (m, $^2J_{3exo,3endo} = 14.0$, $^3J_{3exo,2} = 7.1$ Hz, $^3J_{3exo,4} = 9.3$ Hz, H3*exo*), 2.23 (m, H5), 2.11 (d of d, $^2J_{3endo,3exo} = 13.2$ Hz, $^3J_{3endo,4} = 9.3$, H3*endo*), 2.09* (H6*endo*), 1.93 (m, H7*exo*), 1.62 (m, $^2J_{7endo,7exo}$ = 14.7 Hz, $^3J_{7endo,6endo} = {}^3J_{7endo,6exo} = 9.1$ Hz, H7*endo*), 1.51* (H6*exo*), 1.19 (m, H1), 1.08* (H8), 1.04* (H2); ^{13}C NMR δ_C-$(CDCl_3)$ 78.7 (C9), 55.8 (OMe), 49.5 (C4), 39.3 (C5), 28.7 (C3), 22.7 (C6), 14.9 (C7), 14.5 (C8), 14.0 (C2), 13.0 (C1); LRMS $C_{10}H_{15}{}^{81}BrO$ $M^{\bullet+}$ requires 232, found 232 (1%); $C_{10}H_{15}{}^{79}BrO$ $M^{\bullet+}$ requires 230, found 230 (1%); $C_9H_{11}{}^{81}Br$ $[M - 32]^{\bullet+}$ requires 200, found 200 (15%); $C_9H_{11}{}^{79}Br$ $[M - 32]^{\bullet+}$ requires 198, found 198 (15%); HRMS $C_9H_{11}{}^{81}Br$ $[M - 32]^{\bullet+}$ requires 200.0025, found 200.0039 (19.0%), $C_9H_{11}{}^{79}Br$ $[M - 32]^{\bullet+}$ requires 198.0045, found 198.0037 (20.7%). **9-*syn*-Bromo-5-*endo*-methoxybicyclo[4.2.1]non-2-ene (19).** Compound **19** was identified from a mixture with **18** (ca. 7:3 ratio (**19**/**18**): colorless oil; ^{1}H NMR $\delta_H(CDCl_3)$ 5.84 (m, $^3J_{2,1} = 8.3$ Hz, $^3J_{2,3}$ = 11.7 Hz, $^4J_{2,4endo} = 2.9$ Hz, H2), 5.63 (m, $^3J_{3,2} = 11.7$ Hz, $^3J_{3,4endo} = 3.2$ Hz, $^3J_{3,4exo} = 8.8$ Hz, H3), 4.31 (t, $^3J_{9,1} = {}^3J_{9,6} =$ 6.9 Hz, H9), 3.63 (m, $^3J_{5,4endo} = 10.7$ Hz, $^3J_{5,4exo} = 4.4$ Hz, $^3J_{5,6}$ = 2.5 Hz, H5), 3.35 (s, $W_{h/2} = 0.5$ Hz, OMe), 2.84 (m, $^3J_{1,2} =$ 8.3 Hz, $^3J_{1,8exo} = {}^3J_{1,9} = 7.6$ Hz, H1), 2.72 (m, $^3J_{6,7exo} = {}^3J_{6,9} =$ 6.4 Hz, H6), 2.43* (H4*exo*), 2.26 (m, $^2J_{4endo,4exo} = 16.1$ Hz, $^3J_{4endo,5}$ = 10.7 Hz, $^3J_{4endo,3} = 3.1$ Hz, $^4J_{4endo,2} = 3.1$ Hz, H4*endo*), 2.03* (H8*exo*), 2.00* (H7*endo*), 1.79* (H8*endo*), 1.71* (H7*exo*); ^{13}C NMR $\delta_C(CDCl_3)$ 136.2 (C2), 125.3 (C3), 75.9 (C5), 56.9 (OMe), 55.8 (C9), 47.0 (C6), 41.8 (C1), 30.2 (C4), 29.3 (C8), 22.8 (C7); HRMS $C_{10}H_{15}{}^{81}BrO$ $M^{\bullet+}$ requires 232.0287, found 232.0285 (7.2%); $C_{10}H_{15}{}^{79}BrO$ $M^{\bullet+}$ requires 230.0307, found 230.0337 (8.3%).

Reaction of *exo*-Tricyclo[3.2.2.0^{2,4}]non-6-ene (1) with Bromine in Methanol at 0 °C. A solution of bromine (263 mg, 1.65 mmol) in dry methanol (7 mL) was added dropwise to a solution of **1** (225 mg, 1.87 mmol, 1.1 mol equiv) in dry methanol (10 mL) cooled in an ice bath (0−5 °C). The reaction was stirred for 5 min after which time sodium metabisulfite was added until no bromine color was observed. The solvent was removed under reduced pressure at 0−5 °C, and the residue was extracted with ether. The ether extract was dried over $MgSO_4$, and the solvent was removed under reduced pressure while cooled in an ice bath. The resulting oil (366 mg) was shown by GLC analysis to contain one major product and a number of minor products. Due to the overlap of the compounds on GLC the ratio of products was estimated from a ^{1}H NMR spectrum of the crude reaction mixture. The following compounds were identified: 9-*syn*-bromo-5-*endo*-methoxy-*endo*-tricyclo[4.2.1.0^{2,4}]nonane **18** (30%), 2-*exo*-bromo-4-*exo*-methoxybicyclo[3.2.2]non-6-ene **30** (8%), 4-*endo*-9-*syn*-dimethoxytricyclo[3.3.1.0^{2,8}]nonane (**21**, 7%), 9-*syn*-bromo-5-*endo*-methoxybicyclo[4.2.1]non-2-ene (**19**, 7%), 5-*endo*-9-*syn*-dibromo-*endo*-tricyclo[4.2.1.0^{2,4}]nonane (**2**, 7%), 2-*exo*-4-*exo*-dimethoxybicyclo[3.2.2]non-6-ene (**36**, 6%), 4-*endo*-9-*anti*-dimethoxytricyclo[3.3.1.0^{2,8}]nonane (**20**, 6%), 4-*endo*-bromo-9-*syn*-methoxytricyclo[3.3.1.0^{2,8}]nonane (**17**, 5%), 4-*endo*-bromo-9-*anti*-methoxytricyclo[3.3.1.0^{2,8}]nonane (**16**, 3%), and 2-*exo*-bromo-9-*syn*-methoxybicyclo[3.2.2]non-6-ene (**37**, 3%). A crude separation was effected by radial chromatography on a PEG-coated silica plate (pentane elution). The following compounds were further purified by preparative GLC **18**, **20**, **21**, **16**, **17**, and **36**. Compounds **30** and **37** were isolated from TLC mesh column chromatography on silica. Compounds **2** and **16**−**21** were identified from the ^{1}H and ^{13}C NMR data of the products obtained from the reaction of **1** with Br_2 in methanol at room temperature. **2-*exo*-Bromo-4-*exo*-methoxybicyclo[3.2.2]non-6-ene (30):** colorless oil; ^{1}H NMR $\delta_H(CDCl_3)$ 6.13−6.17 (m, H6, H7), 4.17 (d of d, $^3J_{2,3endo} = 5.2$ Hz, $^3J_{2,3exo} = 11.7$ Hz, H2), 3.29 (s, $W_{h/2} = 0.9$ Hz, OMe), 3.08 (d of d, $^3J_{4,3endo} = 5.2$ Hz, $^3J_{4,3exo}$ =10.8 Hz, H4), 2.73 (m, H1), 2.68 (m, $^2J_{3endo,3exo} =$ 13.2 Hz, $^3J_{3endo,2} = {}^3J_{3endo,4} = 5.3$ Hz, $^4J_{3endo,1} = {}^4J_{3endo,5}$ =1.3 Hz, H3*endo*), 2.50 (m, H5), 2.28 (d of t, $^2J_{3exo,3endo}$ =13.2 Hz, $^3J_{3exo,2} = {}^3J_{3exo,4} = 11.2$ Hz, H3*exo*), 2.18 (t, H8*syn*), 2.02 (t, H9*syn*), 1.63* (H8*anti*), 1.62* (H9*anti*); ^{13}C NMR $\delta_C(CDCl_3)$ 133.7 (C7), 133.3 (C6), 78.8 (C4), 56.3 (OMe), 52.7 (C2), 42.1 (C3), 40.9 (C1), 35.6 (C5), 19.7_2 (C8 or C9), 19.6_8 (C9 or C8); LRMS $C_{10}H_{15}{}^{81}BrO$ $M^{\bullet+}$ requires 232, found 232 (1%); $C_{10}H_{15}{}^{79}$-BrO $M^{\bullet+}$ requires 230, found 230 (1%) $C_9H_{11}{}^{81}Br$ $[M - 32]^{\bullet+}$ requires 200, found 200 (2%) $C_9H_{11}{}^{79}Br$ $[M - 32]^{\bullet+}$ requires 198, found 198 (2%); $C_7H_9{}^{81}Br$ $[M - 58]^{\bullet+}$ requires 174, found 174 (8%); $C_7H_9{}^{79}Br$ $[M - 58]^{\bullet+}$ requires 172, found 172 (8%); HRMS $C_7H_9{}^{79}Br$ $[M - 58]^{\bullet+}$ requires 171.9888, found 171.9890 (11.1%). **2-*exo*-4-*exo*-Dimethoxybicyclo[3.2.2]non-6-ene (36):** colorless oil; ^{1}H NMR $\delta_H(CDCl_3)$ 6.11 (d of d, $^3J_{6,5} = {}^3J_{7,1}$ = 5.6 Hz, $^4J_{6,1} = {}^4J_{7,5} = 3.2$ Hz, H6, H7), 3.31 (s, $W_{h/2} = 0.8$, 2 × OMe), 3.11 (d of d, $^3J_{2,3endo} = {}^3J_{4,3endo} = 5.1$ Hz, $^3J_{2,3exo} = {}^3J_{4,3exo}$ = 11.5 Hz, H2, H4), 2.46 (m, H1, H5), 2.40 (m, $^2J_{3endo,3exo}$ =13.2, $^3J_{3endo,2} = {}^3J_{3endo,4} = 5.2$ Hz, H3*endo*), 1.91 (m, H8*syn*, H9*syn*), 1.61* (H3*exo*), 1.52* (H8*anti*, H9*anti*); ^{13}C NMR $\delta_C(CDCl_3)$ 132.8 (C6, C7), 78.8 (C2, C4), 56.2 (2 × OMe), 36.6 (C3), 35.4 (C1, C5), 19.9 (C8, C9); HRMS $C_{11}H_{18}O_2$ $M^{\bullet+}$ requires 182.1307, found 182.1306 (9.5%). **2-*exo*-Bromo-9-*syn*-methoxybicyclo[3.2.2]non-6-ene (37):** colorless oil; ^{1}H NMR $\delta_H(CDCl_3)$ 6.19 (t, $^3J_{6,5} = {}^3J_{6,7} = 7.8$ Hz, H6), 6.09 (t, $^3J_{7,1} = {}^3J_{7,6} = 7.8$ Hz, H7), 4.32 (d of d, $^3J_{2,3endo} = 5.4$ Hz, $^3J_{2,3exo} = 11.3$ Hz, H2), 3.67 (m, $^3J_{9,5} = {}^3J_{9,8syn} = 4.9$ Hz, $^3J_{9,8anti} = 9.8$ Hz, H9), 3.39 (s, $W_{h/2}$ = 0.6 Hz, OMe), 2.84 (m, H1), 2.78 (m, H3*exo*), 2.62 (m, H5), 2.30 (m, H3*endo*), 2.17* (H8*anti*), 2.12 (m, $^2J_{8syn,\ 8anti} = 14.7$ Hz, $^3J_{8syn,1} = 1.7$ Hz, $^3J_{8syn,9} = 4.6$ Hz, H8*syn*), 1.78 (m, H4*exo*), 1.52* (H4*endo*); ^{13}C NMR $\delta_C(CDCl_3)$ 136.3 (C6), 132.4 (C7), 78.3 (C9), 56.5 (OMe), 55.4 (C2), 42.2 (C1), 36.1 (C3), 34.0 (C5), 27.8 (C8), 27.6 (C4); LRMS $C_{10}H_{15}{}^{81}BrO$ $M^{\bullet+}$ requires 232, found 232 (1%); $C_{10}H_{15}{}^{79}BrO$ $M^{\bullet+}$ requires 230, found 230 (1%); $C_9H_{11}{}^{81}Br$ $[M - 32]^{\bullet+}$ requires 200, found 200 (2%); $C_9H_{11}{}^{79}Br$ $[M - 32]^{\bullet+}$ requires 198, found 198 (2%); $C_7H_9{}^{81}Br$ $[M - 58]^{\bullet+}$ requires 174, found 174 (6%) $C_7H_9{}^{79}Br$ $[M - 58]^{\bullet+}$ requires 172, found 172 (6%). HRMS $C_7H_9{}^{79}Br$ $[M - 58]^{\bullet+}$ requires 171.9888, found 171.9888 (10.8%).

Stability of the Products from Bromination of *exo*-Tricyclo[3.2.2.0^{2,4}]non-6-ene (1) in methanol. A mixture of products obtained from bromination of **1** (103 mg) consisting of **18** (ca. 34%), **20** (ca. 24%), and **21** (ca. 14%) was refluxed in 99.5% methanol-d_4 for 1 h. The solvent was removed under reduced pressure to give a yellow oil (99 mg). Comparison of the ^{1}H and ^{13}C NMR spectra of the products before and after reflux indicated the complete loss of **20** and some loss of **21** (ca. 60%). The appearance of a compound with ^{1}H and ^{13}C NMR data nearly identical to that of **36** was observed in the ^{1}H and ^{13}C NMR spectra of the crude reaction mixture and hence the compound was assigned as 4-*exo*-methoxy-2-*exo*-(trideuteriomethoxy)bicyclo[3.2.2]non-6-ene (**38**) which was not isolated. GCMS analysis of the reaction mixture showed a product with an identical retention time (7.4 min on a Restex

R_{tx}1 30 m × 0.32 mm capillary column) to that of **36** with a molecular ion peak consistent with **38**. This compound was not isolated but was identified from the crude reaction mixture. The following ^{1}H and ^{13}C NMR assignments were made: ^{1}H NMR $\delta_H(CDCl_3)$ 6.11 (d of d, H6, H7), 3.11 (d of d, H2, H4); ^{13}C NMR $\delta_C(CDCl_3)$ 132.8 (C6, C7), 78.7 (C2, C4), 56.1 (OMe), 36.5 (C3), 35.3 (C1, C5), 19.8 (C8, C9). ^{2}H NMR $\delta_D(CCl_4)$ 3.25 (s, OCD_3) HRMS $C_{11}H_{15}{}^2H_3O_2$ $M^{\bullet+}$ requires 185.1495, found 185.1492 (16.9%). Deuterium Incorporation: $C_{11}H_{15}{}^2H_3O_2$ D_0 1%, D_1 0%, D_2 0%, D_3 99%.

Low-Temperature NMR of the Reaction of *exo*-Tricyclo[3.2.2.0^{2,4}]non-6-ene (1) with Bromine in Methanol-*d*$_4$. Bromine (27 mg, 0.17 mmol) in methanol-d_4 (0.2 mL) was added to a solution of **1** (22 mg, 0.18 mmol) in methanol-d_4 (0.4 mL) contained in an NMR tube and cooled in a dry-ice isopropyl alcohol bath. The NMR tube was rapidly transferred to the NMR probe which was precooled to −20 °C. A ^{1}H NMR spectrum run after c.a. 5 min showed no starting material to be present. The sample was slowly warmed to room temperatures and the reaction was monitored by ^{1}H NMR spectroscopy. No significant change in the ^{1}H NMR spectrum was observed on warming. When equilibrated to room temperature the sample was removed, sodium metabisulfite was added, and the solvent was removed under reduced pressure at 0−5 °C. The resulting residue was divided in two; one half was extracted with $CDCl_3$ (0.7 mL) and the other with methanol-d_4 (0.7 mL). A ^{1}H NMR spectrum of the methanol-d_4 extract showed no change from that obtained before workup. ^{1}H and ^{13}C NMR spectra of the $CDCl_3$ extract allowed identification of the deuterated reaction products by comparison with those of the nondeuterated compounds previously isolated. The deuterated analogues of the following products were identified and the product ratios estimated from the ^{1}H and ^{13}C NMR spectra of the $CDCl_3$ extract: **18**, **20**, **21** in a ratio of 10:7:4, respectively.

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Supporting Information Available: ^{1}H, ^{2}H, and ^{13}C NMR spectra (31 pages), tables (7 pages), and structure identification (9 pages) (47 pages total). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the Journal and can be ordered from ACS; see any current masthead page for ordering information.

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