Pergamon

Tetrahedron Vol. 51, No. 29, pp. 8057-8072, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4020/95 $9.50+0.00

0040-4020(95)00420-3

Bromination of *exo*- and *endo*-Tricyclo[3.2.1.0^{2,4}]oct-6-ene

James M. Coxon,* Peter J. Steel, Andrew Burritt and Barry I. Whittington

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

Abstract: Bromination of *exo*- and *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene is initiated at the double bond. This is in contrast to reaction with acid where reaction is initiated preferentially at the cyclopropane. The stationary points on the potential energy surfaces that result from bromine addition to the double bond have been identified by semi-empirical methods. The non-classical bromonium ions are predicted to be less stable than the classical structures. The *exo*-cyclopropylalkene gives *cis* and *trans* 1,2-dibromides along with products which result from reaction of bromine at the *exo* face of the alkene with subsequent rearrangement involving the C2C4 or C2C3 cyclopropyl bonds. The *endo*-cyclopropylalkene similarly reacts with bromine at the *exo* face of the alkene, but 1,2-addition does not compete with rearrangement.

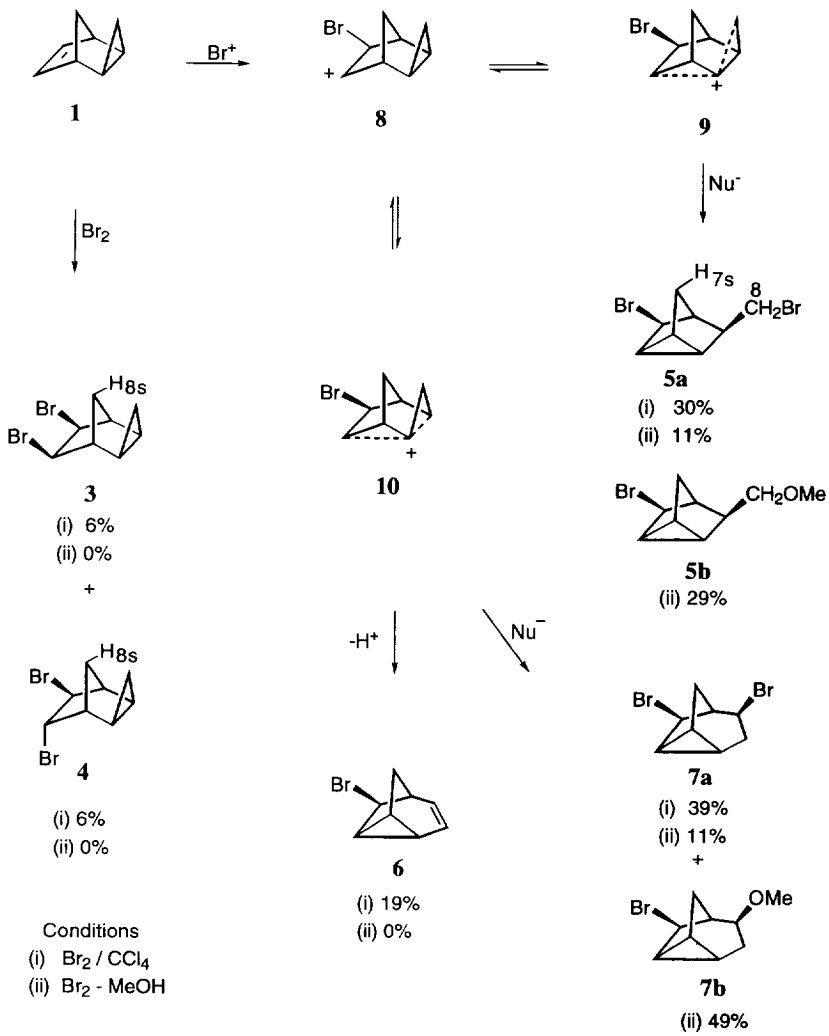
INTRODUCTION

The addition chemistry of cyclopropyl compounds is important as a way to effect 1,3 functionalisation of hydrocarbons. The inherent strain in the cyclopropane ring allows the generation of reactive intermediates by reaction with electrophiles or metals.[1,2] Nature also finds use for cyclopropanes as intermediates in biosynthesis.[3]

We have been interested for some time in the regiochemistry and stereochemistry of the reactions of cyclopropanes. We recently reported the reactions of *exo*- and *endo*-tricyclo[3.2.1.0^{2,4}]octanes with bromine[4] where the differing geometrical constraints imposed on the cyclopropane ring result in different orbital interactions of the cyclopropane with the rest of the hydrocarbon skeleton and thereby influence the course of reaction. Reaction of *exo*-tricyclo[3.2.1.0^{2,4}]octane with the electrophile occurs with inversion at the corner to the C2C4 bond. Nucleophilic attack in the solvent carbon tetrachloride occurs with both inversion and retention. In methanol the initial cation species is sufficiently short lived that it does not relax to the classical cation and nucleophilic attack with inversion competes with skeletal rearrangement. Reaction of *endo*-tricyclo[3.2.1.0^{2,4}]octane with bromine in carbon tetrachloride gives a 1,3-addition product and an addition rearrangement product that are both formed with inversion at the site of attack of both the electrophile and nucleophile. The results contrast with Lambert's study[5] of the reaction of deuterated cyclopropane with bromine where the electrophile would "appear to attack cyclopropane at the edge with retention". We now report the reactions of the unsaturated analogues of these compounds *exo*- and *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (**1**) and (**2**) where competition and interaction between the alkene and cyclopropane result in very different chemistry.

RESULTS AND DISCUSSION

The reaction of *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**1**) with 0.88 molar equivalents of bromine[6] in CCl_4 was instantaneous at room temperature to give 6-*exo*-7-*exo*-dibromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**3**) (6%), 6-*endo*-7-*exo*-dibromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**4**) (6%), 5-*exo*-bromo-3-*exo*-bromomethyltricyclo[2.2.1.$0^{2,6}$]heptane (**5a**) (30%), 6-*exo*-bromotricyclo[3.2.1.$0^{2,7}$]oct-3-ene (**6**) (19%) and 4-*exo*-6-*exo*-dibromotricyclo[3.2.1.$0^{2,7}$]octane (**7a**) (39%) (Scheme 1).



Scheme 1. Bromination of *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**1**).

The identity of 6-*endo*-7-*exo*-dibromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**4**) was determined as follows. A heteronuclear correlation spectrum identified the two CHBr groups H6*exo*, 4.38 ppm (C6, 63.0 ppm) and H7*endo*, 3.93 ppm (C7, 59.5 ppm), the ^{1}H and ^{13}C chemical shifts being consistent with the presence of a bromine substituent.[7] The *trans* stereochemistry of the C6-H and C7-H was established from the presence of only a small coupling between H7*endo* and H6*exo* (3.2 Hz). The coupling between C7-*endo*-H and C8-*syn*-H at 1.12 ppm (3.2 Hz) determines the *endo* orientation of the C7-H.[8] A heteronuclear correlation spectrum shows connectivity between H3*exo* at 0.67 ppm, and H3*endo* at 0.32 ppm, with C3 at 4.2 ppm. Further support for the cyclopropyl stereochemistry can be found in difference nOe spectra. Irradiation at H8s (1.12 ppm), so assigned due to the presence of a coupling with H8a (1.42 ppm, 11.8 Hz) and H7*endo* (3.93 ppm, 3.2 Hz), results in enhancements of H1/H5 (2.55 ppm, 1.0%), H8a (1.42 ppm, 7.4%) and H3*exo* (0.67 ppm, 7.3%).

For 6-*exo*-7-*exo*-dibromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**3**), the ^{1}H NMR and ^{13}C NMR require the product to contain a plane of symmetry. The presence of two CHBr groups at 4.21 ppm (C6, C7 56.7 ppm) with coupling to H8s (1.06 ppm, 2.3 Hz) requires C6-H and C7-H to be *endo*.[9] The presence and configuration of an *exo* cyclopropyl group follow from the chemical shifts (H3*exo* 0.72 ppm, H3*endo* 0.38 ppm, C3 6.1 ppm) and the couplings $^{2}J_{3endo,3exo}$ 6.3 Hz, $^{3}J_{3endo,2} = {}^{3}J_{3endo,4}$ 7.0 Hz, $^{3}J_{3exo,2} = {}^{3}J_{3exo,4}$ 3.0 Hz, these values being comparable with those for *exo*-tricyclo[3.2.1.$0^{2,4}$]octane.[1a]

A heteronuclear correlation spectrum of 4-*exo*-6-*exo*-dibromotricyclo[3.2.1.$0^{2,7}$]octane (**7a**) identified the CHBr groups H4*endo*, 4.14 ppm (C4, 47.8 ppm) and H6, 4.30 ppm (C6, 55.2 ppm). H6 is a singlet, $W_{h/2}$ 3 Hz, consistent with its stereochemistry as *endo*.[10] This is confirmed by the nOe experiments reported below. The magnitude of the coupling from C4-H at 4.14 ppm to H3*endo* (2.52 ppm, 7.0 Hz), H3*exo* (2.39 ppm, 7.0 Hz), H8a (2.20 ppm, 1.5 Hz), along with a further coupling to H5 (2.55 ppm, 1.5 Hz) compares with those observed in the analogue 2-methyltricyclo[3.2.1.$0^{2,7}$]octan-6-*exo*-ol.[11] The stereochemistry of the C4-H was determined from difference nOe spectra. Irradiation at H4 (4.14 ppm) gave enhancements at H6*endo* (4.30 ppm, 4.0%), H5/H3*endo* (ca. 2.54 ppm, 5.0% total) and H3*exo* (2.39 ppm, 0.6%). In addition, irradiation at H3*endo* and H5 at 2.54 ppm gave enhancements at H6*endo* (4.30 ppm, 1.0%), H4*endo* (4.14 ppm, 4.3%), H3*exo* (2.39 ppm, 8.1%) and H2 (1.00 ppm, 1.0%). The large enhancement from H4 to H6*endo* (4.0%) confirms the assignment of the C4*endo*-H at 4.14 ppm.[12]

For 5-*exo*-bromo-3-*exo*-bromomethyltricyclo[2.2.1.$0^{2,6}$]heptane (**5a**)[13] the relative stereochemistry of the CH_2Br group and C5Br as *cis* was established from a difference nOe spectrum. Irradiation at H8a and H8b (3.30 - 3.15 ppm) resulted in enhancements at H4 (2.22 ppm, 1.6%), H3 (2.12 ppm, 2.6%), H2 (1.30 ppm, 1.6%) and in particular H7s (1.52 ppm, 5.1%). The relative stereochemistry of C5-H similarly followed from a difference nOe spectrum. Irradiation at H5 (3.96 ppm) gave enhancements at H4 (1.4%), H6 (1.67 ppm, 1.3%) and specifically with H3 (4.7%) but not of the CH_2Br (3.28 ppm and 3.18 ppm). The coupling between the cyclopropyl protons ($^{3}J_{1,2} = {}^{3}J_{1,6} = {}^{3}J_{2,6}$ 5.2 Hz), along with the Cl, C2 and C6 methines as determined by an APT spectrum, requires the presence of a cyclopropyl group.

6-*exo*-Bromotricyclo[3.2.1.$0^{2,7}$]oct-3-ene (**6**) was identified by comparison of the observed ^{1}H NMR spectrum with that previously reported.[14]

For the reaction of **1** with bromine in CCl_4, the electrophile and nucleophile cannot be distinguished and hence no comment can be made on the trajectory of attack of either the electrophile or the nucleophile in the formation of **4** and **7a**. For formation of **3** both the electrophile and the nucleophile must however attack *exo* and similarly for **5a** the electrophile must attack *exo*. In order to determine the separate trajectories of the

electrophile and nucleophile in the formation of **4** and **7a** the reaction of **1** with bromine was repeated using methanol as the reaction solvent. In this case the methanol can compete with bromide as nucleophile. This gave four products[15] in 84% isolated yield, namely 5-*exo*-bromo-3-*exo*-bromomethyltricyclo-[2.2.1.0^{2,6}]heptane (**5a**) (11%), 4-*exo*-6-*exo*-dibromotricyclo[3.2.1.0^{2,7}]octane (**7a**) (11%), 5-*exo*-bromo-3-*exo*-methoxymethyltricyclo[2.2.1.0^{2,6}]heptane (**5b**) (29%) and 6-*exo*-bromo-4-*exo*-methoxytricyclo-[3.2.1.0^{2,7}]octane (**7b**) (49%).

For both **5b** and **7b** the coupling constants for each of the protons in the ^{1}H NMR spectrum are of the same magnitude as those observed with the corresponding dibromides, and hence is consistent with the same carbon skeleton and stereochemistry as previously observed for **5a** and **7a**. The regiochemistry of the methoxy group in **5b**[16] and **7b**, was determined by examination of the chemical shift differences in the ^{1}H and ^{13}C NMR spectra with **5a** and **7a**.[17] For **7b**, a heteronuclear correlation spectrum identified all of the one bond carbon-proton connectivities and the changes in chemical shift upon substitution of a bromine by methoxy are consistent with the presence of a methoxy group at C4. The relative stereochemistry (*endo*) of C4-H and C6-H was established from a difference nOe spectrum. Irradiation of H6 at 4.22 ppm gives enhancements at H4 (3.27 ppm, 3.2%), H5 (2.44 ppm, 1.6%), H3*endo* (2.15 ppm, 0.8%) and H7 (1.77 ppm, 1.6%) but not the methoxy methyl at 3.23 ppm.

The reaction of **1** with bromine is rapid compared with reaction of bromine with the saturated analogues where reaction necessarily occurs at the cyclopropyl bond.[4] The presence of 6-*exo*-bromo-4-*exo*-methoxytricyclo[3.2.1.0^{2,7}]octane (**7b**) and 5-*exo*-bromo-3-*exo*-methoxymethyltricyclo[2.2.1.0^{2,6}]heptane (**5b**) is only consistent with initial attack by the electrophile, bromine, at the double bond and not at the cyclopropane (Scheme 1). The preference for bromine to attack at a double bond can be rationalised by a consideration of the stability of the possible intermediate cations. The ion formed by reaction of bromine with an alkene is more stable than that formed by reaction with cyclopropane, whether edge or corner brominated (corner shown in the figure). The energy differences between the starting structures and the carbocations reflect the activation energies for their formation with $\Delta E^2 > \Delta E^1$ (Figure 1).

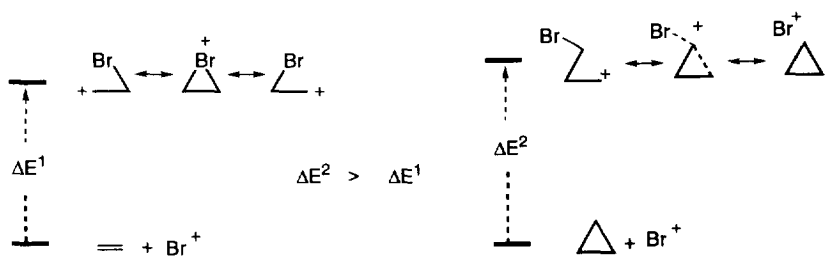


Figure 1. Addition of Br^+ to an alkene and a cyclopropane

The intermediacy of bromonium ions in the reaction of bromine with alkenes was first proposed in 1937.[18] It was not until 1985 that the first X-ray of such a species was reported.[19] The bromonium ion tribromide complex formed from adamantylideneadamantane is slightly asymmetric as a result of perturbation caused by the positioning of the anion in the crystal with Br-C bond lengths of 2.116(6) and 2.194(6) Å and the C-C bond of 1.497(8) Å. The internal angles of the ring were 40.6(2)° at Br and 72.5(3) and 66.9(3)° at

the C atoms. Few calculations have been conducted on bromonium cations and it seemed desirable to see if semi-empirical calculations could predict the selectivity observed for such complex systems as **1** and **2**.

Previous MNDO and AM1 *semi*-empirical molecular orbital studies[20] of cations formed by reaction of simple symmetrically substituted alkenes, such as (E)-but-2-ene, 1,2-dimethylbut-2-ene, and ethene with bromine support symmetrically bridged bromonium ions as intermediates. The classical ions are calculated to be higher in energy on the potential energy surface. These calculations are supported by ab initio studies of $C_2H_4Br^+$.[21] For simple substituted alkenes where a tertiary cation can form, semi-empirical (MNDO) methods predict the classical tertiary ion, to be an energy minimum. For alkenes where structural features do not allow the formation of a tertiary ion the carbocation intermediate is calculated to be a partially bridged. For example for propene, 2-methylpropene, and 2-methylbut-2-ene, MNDO calculations predict distorted classical bromo carbocations as the lowest energy stationary points on the potential energy surface.[22]

We have investigated the non-classical bromonium ions and the classical cations by MNDO, AM1 and PM3 methods for addition of Br^+ to the symmetric double bonds of **1** and **2** (see Figures 2 and 3). On all surfaces the classical cations are minima and lower in energy than the corresponding non-classical bromonium ions. The non-classical ions were characterised somewhat differently by the three semi-empirical Hamiltonians but the bond lengths were remarkably consistent with those reported for the bromonium ion tribromide complex formed from adamantylideneadamantane.

For the alkene **1**, semi-empirical calculations at the AM1, PM3 and MNDO levels of theory show the *exo* bromonium ion (C-Br distances of 2.115 and 2.111 Å, AM1) is higher in energy than the classical cation with calculated distances between Br and C6 and C7 of 1.930 and 2.802 Å (AM1). For this reason in Scheme 1 the ion formed initially from reaction of Br^+ and **1** is shown as a classical ion **8**. The symmetrical *exo* bromonium ion **11** is calculated as a minimum at the AM1 and MNDO levels of theory, but at higher energy than **8**, and is characterised as a transition state at the PM3 level of theory. At the AM1 level of theory *exo*-classical ion **8** is almost identical in energy to the *endo* classical ion **13** (calculated C6 and C7 distances to bromine of 1.916 and 2.866 Å, AM1) though PM3 and MNDO calculations show the *exo* ion is slightly lower in energy than the *endo* ion.

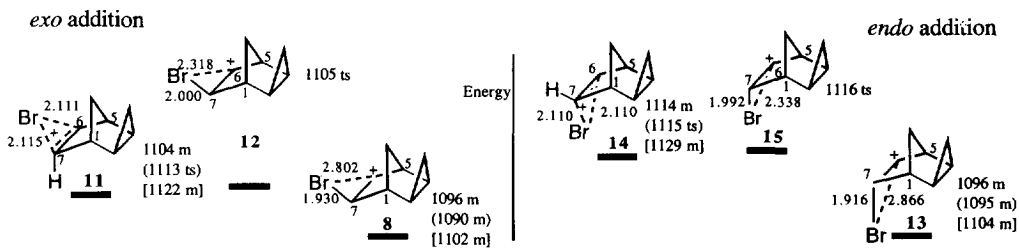
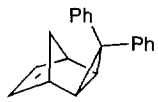


Figure 2. Stationary points on the potential energy surface AM1 (PM3) [MNDO] for the addition of Br^+ to **1** (Energies in kJ mol^{-1}. m = minimum, ts = transition state).

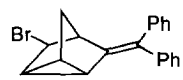
At the PM3 level of theory the non-classical ion **14** is calculated as a transition state and compares to the similar calculation of **11**. At the AM1 level of theory the transition states **12** and **15** between **8** and **11** and

between **13** and **14** were characterised as *ca.* 1-2 kcal mol^{-1} higher in energy than the symmetrical bromonium ions **11** and **14** (see Figure 2).

In the reaction of **1** with bromine, rearrangement of an initially formed carbocation **8** can occur with participation of the C2C3 cyclopropyl bond to give **9**,[23] which when captured by bromide gives **5a.** With participation of the internal C2C4 cyclopropyl bond **8** can rearrange to give **10** that may undergo loss of a proton to give **6**, or attack by nucleophile to form **7**. Such a mechanism has been proposed to explain the results from the acetolysis of the bromobenzenesulphonates of *exo*-tricyclo[3.2.1.$0^{2,4}$]octan-6-*exo*- and 6-*endo*-ol.[24] A similar propensity towards rearrangement analogous to the formation of **5** is found in the reaction of bromine to 3,3-diphenyl-*exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene[9] (**16**) the product of this reaction being 5-*exo*-bromo-3-diphenylmethylenetricyclo[2.2.1.$0^{2,6}$]heptane (**17**).



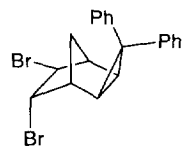
16



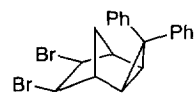
17

It is notable that in methanol the formation of the 1,2-addition products **3** and **4** is suppressed. Nucleophilic attack by solvent or bromide on an initially formed *exo* ion no longer competes with rearrangement. Bromide ion attack on the rearranged carbocations to give **5a** and **7a** remains competitive with capture by solvent to give **5b** and **7b**. The ratio of **5a**:**5b** (11:29) and **7a**:**7b** (11:49) contrasts with the reaction of *exo*- and *endo*-tricyclo[3.2.1.$0^{2,4}$]octane with bromine in methanol, where methanol is preferentially captured (>10:1). Failure to detect the methoxy analogue of **4** means that it is not possible from these experiments to establish the trajectory of electrophile and nucleophile in the formation of **4**.

In the reaction of *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**1**) with bromine in carbon tetrachloride, the possibility that the unrearranged 1,2-addition dibromides **3** and **4** arise from bromine radical attack at the double bond should also be considered. 1,2-Bromine addition, to yield the *cis-exo* dibromide, is surprising in view of the known reaction of norbornene with bromine.[25] Furthermore, the reaction of bromine in the presence of light with 3,3-diphenyl-*exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**16**) gives[26] a 4:1 mixture of 6-*endo*-7-*exo*- and 6-*exo*-7-*exo*- dibromo-3,3-diphenyl-*exo*-tricyclo[3.2.1.$0^{2,4}$]octanes (**18**) and (**19**).



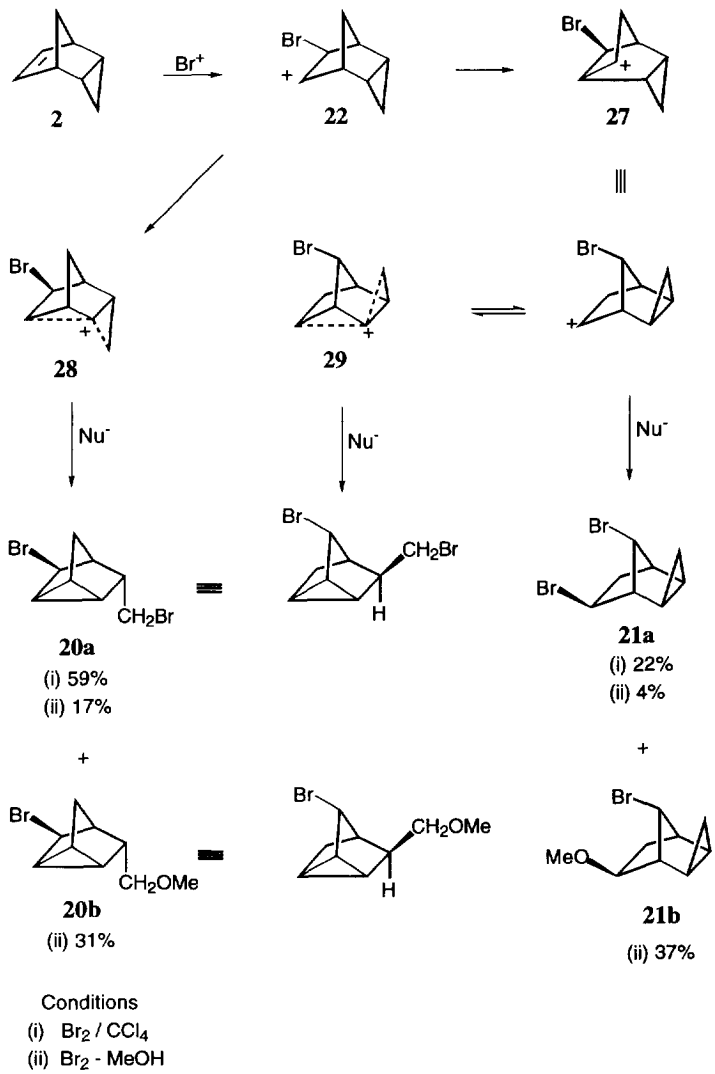
18



19

Although radical reactions of bromine with cyclopropanes are known to occur rapidly in nonpolar solvents[26] the possibility for radical induced addition was minimised by carrying out the reactions in the dark. As CCl_4 was the reaction solvent[27] and the probability of collision with solvent is greater than with bromine, at least some chloride containing products would be expected if the reaction were radical in nature.[28] In our study no products containing chlorine were observed. The role of electron transfer in the reaction of strained systems with bromine has yet to be elucidated.[29]

Reaction of *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**2**) with bromine in carbon tetrachloride gave two major products (Scheme 2); 5-*exo*-bromo-3-*endo*-bromomethyltricyclo[2.2.1.$0^{2,6}$]heptane (**20a**) (59%) and 6-*exo*-8-*anti*-dibromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**21a**) (22%) in addition to three minor, unidentified compounds (5%, 6% and 7%).



Scheme 2. Bromination of *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene **2.**

5-*exo*-Bromo-3-*endo*-bromomethyltricyclo[2.2.1.$0^{2,6}$]heptane (**20a**) was identified from the proton-proton homonuclear correlation spectrum (COSY). The two carbons substituted with bromine groups, C5 (53.6 ppm) and C8 (32.5 ppm), were assigned from a heteronuclear correlation spectrum; C5 and C8 exhibiting connectivity with H5 at 4.04 ppm, and H8a and H8b at 3.23 ppm and 3.12 ppm respectively. The

C6-H is a broad singlet consistent with the assigned stereochemistry.[30] The relative stereochemistry of the CH_2Br group and C5-H was established from a difference nOe spectrum. Irradiation at H8a, H8b (3.25-3.10 ppm) gave enhancements at H5 (4.04 ppm, 12.6%), H4 (2.10 ppm, ca. 1.0%), H3 (2.04 ppm, 3.2%) and H2 (1.23 ppm, 2.3%). The observed couplings between the cyclopropyl protons H1, H2 and H6 ($^3J_{1,2} = {}^3J_{2,6}$ 5.0 Hz) and ATP spectrum established C1, C2 and C6 as methine carbons confirming the presence of an endocyclic cyclopropyl group.

The identity of 6-*exo*-8-*anti*-dibromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**21a**) follows from the observed proton-proton couplings (COSY spectrum). A heteronuclear shift correlation spectrum identified the two CHBr groups H6*endo*, 3.98 ppm (C6, 47.9 ppm) and H8, 3.78 ppm (C8, 47.7 ppm). The presence of an *exo*-cyclopropyl group was determined by comparison with the coupling and chemical shift data[31] with *exo*-tricyclo[3.2.1.$0^{2,4}$]octane.[1a] The *endo* stereochemistry of C6-H was established from the couplings to H7*endo* (2.33 ppm, 8.0 Hz), H7*exo* (2.58 ppm, 4.5 Hz) and H8 (3.78 ppm, 1.5 Hz). Coupling from the C8**H**Br to H6 (1.5 Hz), H7*endo* (2.3 ppm, 1.8 Hz), Hl (2.50 ppm, 1.6 Hz) and H5 (2.79 ppm, 1.6 Hz), in addition to a difference nOe spectrum in which irradiation at H8s (3.78 ppm) gives enhancements at H5 (2.79 ppm, 2.8%), Hl (2.50 ppm, 2.1%) and H3*exo* (0.78 ppm, 10.7%) identifies this proton as *syn*.

To identify the position of attack by electrophilic bromine, the reaction of *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**2**) with bromine in methanol was examined. This reaction gave four products, namely the previously observed 5-*exo*-bromo-3-*endo*-bromomethyltricyclo[2.2.1.$0^{2,6}$]heptane (**20a**) (17%) and 6-*exo*-8-*anti*-dibromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**2a**) (4%), along with 5-*exo*-bromo-3-*endo*-methoxymethyltricyclo-[2.2.1.$0^{2,6}$]heptane (**20b**) (31%) and 8-*anti*-bromo-6-*exo*-methoxy-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**21b**) (37%).[15] For both **20b** and **21b**, the magnitude of the coupling between the protons is the same as that observed with the dibromides **20a** and **21a**, the only significant differences in the spectra being the chemical shift changes induced by substitution of a bromine with a methoxy.

For 5-*exo*-bromo-3-*endo*-methoxymethyltricyclo[2.2.1.$0^{2,6}$]heptane (**20b**), a comparison of the chemical shift data[32] with the dibromide **20a** establishes the methoxy group as being at C8. The relative stereochemistry of the C8H_2-OMe and H5 was confirmed from a difference nOe spectrum. Irradiation at H8a, H8b and the methoxy methyl gave enhancements of a singlet at 4.22 ppm assigned to H5*endo* (7.4%), H4 (2.10 ppm, 1.8%), H3 (1.96 ppm, 5.2%), H6 (1.52 ppm, 1.2%) and H2 (1.20 ppm, 2.4%).

For 8-*anti*-bromo-6-*exo*-methoxy-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**21b**), comparison of the chemical shift data with that of the corresponding dibromide **21a**, was consistent with the presence of the methoxy group at C6. The *endo* stereochemistry of the C6-H follows from coupling to H7*endo* (1.98 ppm, $^3J_{6endo,7endo}$ 6.4 Hz), H7*exo* (2.08 ppm, $^3J_{6endo,7exo}$ 3.7 Hz) and H8s (3.68 ppm, $^4J_{6endo,8s}$ 1.6 Hz). Addition of ArSCl to *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**2**) similarly gives only products resulting from attack of the double bond.[33] The presence of **20b** and **21b** in the reaction of **2** with bromine in methanol requires initial electrophilic attack to occur at the *exo* face of the double bond to give an ion **22**. Rearrangement of **22** can occur with participation of the C2C3 cyclopropyl bond to give **28**, or by Wagner Meerwein rearrangement and participation of the cyclopropyl bond to give **29.** Attack by bromide or methanol on either **28** or **29** gives **20a** or **20b** respectively.

Semi-empirical calculations at the AM1, PM3 and MNDO levels of theory (Figure 3) show that the *exo* classical carbocation **22** (calculated C6 and C7 distances of 1.937 and 2.777 Å, AM1) is lower in energy than the *exo* nonclassical ion **23** (C-Br distances of 2.115 and 2.113 Å, AM1). For this reason in Scheme 2 the ion formed initially from reaction of Br^+ and **2** is shown as a classical ion **22**. The symmetrical *exo*

bromonium ion **23** is calculated as a minimum at AM1 and MNDO levels of theory, but higher than the classical ion **22**, and a transition state at the PM3 level of theory. At the AM1 level of theory the transition state **24** between **23** and **22** is ca. 6 kJ mol^{-1} higher in energy than the cation **23.**

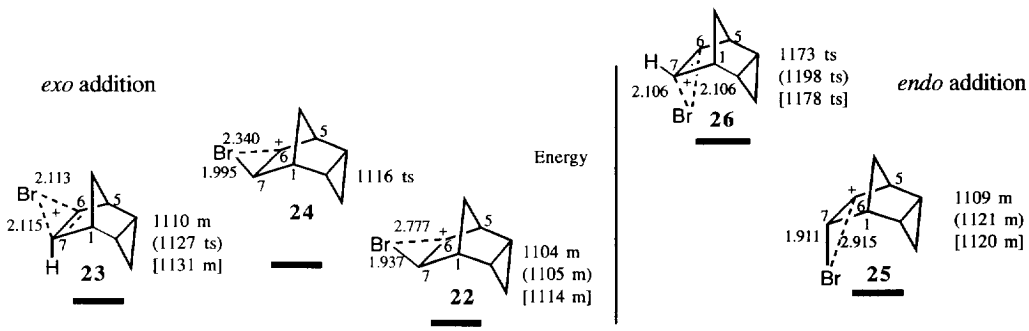


Figure 3. Stationary points on the potential energy surface AM1 (PM3) [MNDO] for the addition of Br^+ to **2** (Energies in kJ mol^{-1})

At all three levels of theory *exo*-classical ion **22** is significantly lower in energy than the *endo* classical ion **25** or *endo* nonclassical ion **26.** The *endo* non-classical ion **26** (calculated C6 and C7 distances to bromine of 2.106 Å, AM1) is calculated at all levels of theory to be a transition state between **25** and its enantiomer and to be substantially higher (>ca 60 kJ mol^{-1}) in energy than the *endo* classical ion **25** as a result of the interaction of the bromine atom and the C4*endo*-**H**. The calculations at all levels of theory support the experimental results that *exo* attack of bromine occurs exclusively.

The *exo* ion **22** formed by electrophilic attack at the alkene can rearrange either by a Wagner Meerwein rearrangement to cation **27** or by involvement of the C2C3 *endo* cyclopropyl bond to **28** which can be captured by a nucleophile to give **20.** Cation **27** could also rearrange to **29** and hence to **20**. These two reasonable routes to **20** are not differentiated by the experiments. This reaction is mechanistically similar to the reaction of **2** with ArSCl[35] and the reaction of 6-*exo*-epoxy-*endo*-tricyclo[3.2.1.$0^{2,4}$]octane with HBr.[34] However the bromination of hydrocarbon **2** is unusual in that, unlike the two previously mentioned reactions, no tricyclo[3.2.1.$0^{2,7}$]octanes were observed. To check for the presence of a 4-*exo* substituted 6-*exo*-bromotricyclo[3.2.1.$0^{2,7}$]octane (**7**), the NMR of the crude reaction mixture from the bromination of hydrocarbon **2** was compared with the ^1H and ^{13}C NMR spectra of **7a** or **7b** from reaction of hydrocarbon **1** with bromine in either CCl_4 or methanol. There was no evidence for the presence of either **7a** and **7b** in the reaction mixture. This indicates that interaction of the C2C4 cyclopropyl bond to give the cation analogous to **10** does not occur in this reaction system.

The angle, α, between the planes of the bromonium ion and that defined by C1-C7-C6-C5 for the non-classical structures increases in the order (AM1) **23**, 113.5°; **11**, 114.1°; **14**, 116.5°; **26**, 124.5°[35] reflecting the congestion of the hydrocarbon framework. The methylene bridge in the *exo* bromonium ions **23** and **11** provides less congestion than the C2HC4H in the *endo* bromonium ion **14** and the C3-*endo* methylene in **26.** In **26** the steric interaction of the bromine with the C3-*endo*-H is at a maximum and accounts for this being a transition structure. For the AM1, PM3 and MNDO methods **26** is substantially

destabilised by steric interactions with C3-*endo*-H relative to the corresponding classical cation **25** where this steric interaction is reduced. These values of α compare with an equivalent angle of 102.7° for the ethylene bromonium ion.[36]

The activation energy for interconversion of the classical ions parallels the increase in angle (α) of the transition bromonium ion structures (See figures 2 and 3). As this angle increases the nonclassical transition species increase in energy relative to the classical ions. The stabilisation possible by bridging is compromised by steric interference. The nature of the potential energy surface is expected to be reflected in the trajectory of electrophilic attack where attack perpendicular to the plane of the double bond is disfavoured. The calculations are consistent with *exo* attack of the electrophile being favoured. Steric interactions of the electrophile with the C8 methylene and/or the C3 methylene in **1** and C2-H/C4-H of **2** preclude the symmetrical non-classical ion being the lowest energy intermediate on the potential energy surface.

CONCLUSION

For reaction of **1** and **2** with bromine, all three semi-empirical MO methods predict bromonium ion formation to be of higher energy than the corresponding open classical cations due to steric interactions. *exo*-Addition of the electrophile to **2** is calculated to be substantially favoured over *endo* addition and this finds parallel with experiment. The "double minima" energy profiles predicted contrast to predictions for simple substituted and unsubstituted ethylene systems. For **1** the *exo* and *endo* classical structures are calculated to be close in energy and lower in energy than the nonclassical structures. Semi-empirical calculations show the PM3 method underestimates the stability gained from bromonium ion formation relative to the AM1 and MNDO methods. The observation of both *trans* and *cis* addition of bromine to **1** is consistent with the intermediacy of classical cations. The other products of reaction require *exo* addition of electrophile.

Bromine reacts regiospecifically with *exo*- and *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**1**) and (**2**) at the double bond contrasting with the chemistry with proton acids[1] and finding a closer parallel with the reactions of mercuric acetate. Bromination of **2** results in products from *exo* addition of the electrophile to the double bond. This is followed by skeletal rearrangement involving intramolecular reaction with the C1C2 or C2C3 bonds before nucleophilic capture by bromide. For the reaction of **1**, the initially formed ion from attack of the electrophile at the double bond is captured by bromide to give equal quantities of *trans* and *cis* 1,2-dibromide (12%) competing with intramolecular rearrangement involving the C2C4 and C2C3 but not C1C2 bonds.

EXPERIMENTAL

NMR spectra were recorded on a Varian XL-300 spectrometer equipped with a 5 mm probe and operating at 300 MHz and 75 MHz for ^{1}H and ^{13}C, respectively. 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.[37] All other NMR experiments were recorded using standard pulse sequences and parameters available with the XL-300 systems. Mass spectra were recorded on an AEI MS902 spectrometer. Radial chromatography was performed on a chromatotron (Harrison and Harrison) using Merck grade 60PF_{254} silica gel. A Hewlett Packard 5890A glc was used in both analytical and

preparative modes. For preparative separations 1.5% OV-17 and 1.95% QF-1 on chromosorb W in a column of 5mm external diameter and length 3m was used.

***Reaction of exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (1) *with bromine in* CCl_4** To a stirred solution of *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**1**) (220 mg) in CCl_4 (10 ml) was added bromine (292 mg, 0.88 molar equivalent) in CCl_4 (5 ml). The mixture was stirred for 3 minutes before removal of the solvent and unreacted starting material under reduced pressure to give a pale yellow oil (466 mg, 96%). Glc identified five major products. Separation was effected by radial chromatography (SiO_2, pentane) to give 6-*exo*-bromotricyclo[3.2.1.$0^{2,7}$]oct-3-ene (**6**) (19%), 6-*endo*-7-*exo*-dibromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**4**) (6%), 4-*exo*-6-*exo*-dibromotricyclo[3.2.1.$0^{2,7}$]octane (**7a**) (39%), 5-*exo*-bromo-3-*exo*-bromomethyltricyclo[2.2.1.$0^{2,6}$]heptane (**5a**) (30%) and 6-*exo*-7-*exo*-dibromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]-octane (**3**) (6%). **6-*exo*-Bromotricyclo[3.2.1.$0^{2,7}$]oct-3-ene (6)**: ^{1}H NMR δ_H ($CDCl_3$) 5.87-5.80 (m), H3, H4; 3.64 (s), $W_{h/2}$ = 2 Hz, H6; 2.75 (t), $^3J_{5,8anti}$ 6.0 Hz, $^3J_{4,5}$ 6.5 Hz, H5; 2.25 (m), $^2J_{8anti,8syn}$ 11.8 Hz, $^3J_{8anti,1}$ 2.4 Hz, $^3J_{8anti,5}$ 6.0 Hz, H8*anti*; 1.74 (s), $W_{h/2}$ 9 Hz, H2, H7; 1.68 (t of d), $^3J_{1,2} = {}^3J_{1,7}$ 6.0 Hz, $^4J_{1,5}$ 1.8 Hz, H1; 0.88 (d), $^2J_{8anti,8syn}$ 11.8 Hz, H8*syn*. The ^{1}H NMR of this compound has previously been reported.[14] ^{13}C NMR δ_C ($CDCl_3$) 127.1, C4; 123.0, C3; 56.2, C6; 42.0, C5; 25.4, C8; 22.1, C7; 20.0, C2; 15.1, Cl. **6-*endo*-7-*exo*-Dibromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (4)**: ^{1}H NMR δ_H ($CDCl_3$) 4.38 (t), $^3J_{5,6} = {}^3J_{6,7}$ 3.2 Hz, H6; 3.93 (t), $^3J_{7,6} = {}^4J_{7,8syn}$ 3.2 Hz, H7; 2.57 (s), $W_{h/2}$ = 3.8 Hz, Hl; 2.54 (s), $W_{h/2}$ = 10 Hz, H5; 1.42 (d of t), $^2J_{8anti,8syn}$ 11.8 Hz, $^4J_{8anti,2} = {}^4J_{8anti,4}$ 1.3 Hz, H8*anti*; 1.12 (d of d), $^2J_{8anti,8syn}$ 11.8 Hz, $^4J_{7,8syn}$ 3.2 Hz, H8*syn*; 0.92, H2,4; 0.67 (d of t), $^2J_{3exo,3endo}$ 6.3 Hz, $^3J_{3exo,2} = {}^3J_{3exo,2} = {}^3J_{3exo,4}$ 3.2 Hz, H3*exo*; 0.32 (m), $^2J_{3endo,3exo}$ 6.3 Hz, $^3J_{3endo,2} = {}^3J_{3endo,4}$ 7.1 Hz, H3*endo*. ^{13}C NMR δ_C ($CDCl_3$) 63.0, C6; 59.5, C7; 47.1, Cl; 43.9, C5; 24.6, C8; 13.8, 11.2, C2, C4; 4.22, C3. **4-*exo*-6-*exo*-Dibromotricyclo[3.2.1.$0^{2,7}$]octane (7a)**: ^{1}H NMR δ_H ($CDCl_3$) 4.30 (s), $W_{h/2}$ = 3 Hz, H6*endo*; 4.14 (m), $^3J_{4endo,3exo} = {}^3J_{4endo,3endo}$ 7.0 Hz, $^3J_{4endo,5} = {}^4J_{4endo,8anti}$ 1.6 Hz, H4*endo*; 2.55 (s), $W_{h/2}$ 6 Hz, H5; 2.52 (m,), $^2J_{3exo,endo}$ 15.5 Hz, $^3J_{3endo,2}$ 3.4 Hz, $^3J^{\circ}{}_{4endo,3endo}$ 7.0 Hz, H3*endo*; 2.39 (m), $^2J_{3exo,3endo}$ 15.5 Hz, $^3J_{3exo,2}$ 1.9 Hz, $^3J_{3exo,4endo}$ 7.0 Hz, H3*exo*; 2.20 (s), $W_{h/2}$ = 5 Hz, H8*syn*,H8*anti*; 1.85 (m), $^3J_{7,1} = {}^3J_{7,2}$ 6.6 Hz, $^4J_{7,5} = {}^4J_{7,8syn}$ 1.3 Hz, H7; 1.67 (s), $W_{h/2}$ = 11 Hz, H1; 1.00 (m), $^3J_{2,1} = {}^3J_{2,7}$ 7.0 Hz, $^3J_{2,3endo}$ = 3.4 Hz, $^3J_{2,3exo}$ 1.9 Hz, H2. ^{13}C NMR δ_C ($CDCl_3$) 55.2, C6; 49.8, C5; 47.8, C4; 29.6, C3; 25.3, C7; 23.0, C8; 18.4, C2; 18.0, Cl. MS: $C_8H_{10}Br_2$ requires $M^+\cdot$ 267.9111; Found $M^+\cdot$ 267.9110. **5-*exo*-Bromo-3-*exo*-bromomethyltricyclo[2.2.1.$0^{2,6}$]heptane (5a)**: ^{1}H NMR δ_H ($CDCl_3$) 3.96 (s) $W_{h/2}$ = 3.2 Hz, H5; 3.28 (d of d), $^2J_{8a,8b}$ 10.1 Hz, $^3J_{8a,3}$ 7.2 Hz, H8a; 3.18 (d of d), $^2J_{8b,8a}$ 10.1 Hz, $^3J_{8b,3}$ 8.7 Hz, H8b; 2.22 (s), $W_{h/2}$ = 5 Hz, H4; 2.12 (d of d), $^3J_{3,8a}$ 7.2 Hz, $^3J_{3,8b}$ 8.7 Hz, H3; 2.05 (d), $^2J_{7anti,7syn}$ 11.8 Hz, H7*anti*; 1.67 (t), $^3J_{6,1} = {}^3J_{6,2}$ 5.2 Hz, H6; 1.52 (d), $^2J_{7anti,7syn}$ 11.8 Hz, H7*syn*; 1.44 (t), $^3J_{1,2} = {}^3J_{1,6}$ 5.0 Hz, H1; 1.30 (t), $^3J_{2,1} = {}^3J_{2,6}$ 5.0 Hz, H2. ^{13}C NMR δ_C ($CDCl_3$) 55.9, C5; 46.1, C3; 40.9, C4; 32.4, C8; 27.0, C7; 20.8, C6; 18.8, C2; 11.7, Cl. MS: $C_8H_{10}Br_2$ requires $M^+\cdot$ 267.9111; Found $M^+\cdot$ 267.9100. **6-*exo*-7-*exo*-Dibromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (3)**: ^{1}H NMR δ_H ($CDCl_3$) 4.21 (d), $^4J_{6endo/7endo,8s}$ 2.3 Hz, H6*endo*, H7*endo*; 2.63 (s), $W_{h/2}$ = 3 Hz, H1, H5; 1.65 (d), $^2J_{8anti,8syn}$ = 11.8 Hz, H8*anti*; 1.06 (d of t), $^2J_{8syn,8anti}$= 11.8 Hz, $^4J_{8syn,6endo} = {}^4J_{8syn,7endo}$ 2.3 Hz, H8*syn*; 0.88 (d of d), $^3J_{2/4,3exo}$ = 3.0 Hz, $^3J_{2/4,3endo}$ = 7.0 Hz, H2,4; 0.72 (d of t), $^2J_{3exo,3endo}$ 6.3 Hz, $^3J_{2,3exo} = {}^3J_{4,3exo}$ 3.0 Hz, H3*exo*; 0.38 (m), $^2J_{3exo,3endo}$ 6.3 Hz, $^3J_{2,3endo} = {}^3J_{4,3endo}$ 7.0 Hz, H3*endo*. ^{13}C NMR δ_C ($CDCl_3$) 56.7, C6,7; 47.8, Cl,5; 22.4, C8; 14.8, C2,4; 6.1, C3.

Reaction of 1 with bromine in methanol To a solution of *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**1**) (170 mg) in anhydrous methanol (15 ml) was added bromine (225 mg, 0.88 molar equivalent) in methanol (2 ml). The mixture was stirred for 2 minutes and then CCl_4 (5 ml) added. The mixture was washed with water, the organic layer separated, dried over $MgSO_4$ and the solvent removed under reduced pressure to give a clear, colourless oil (268 mg, 84%), shown to contain 4-*exo*-6-*exo*-dibromotricyclo[3.2.1.$0^{2,7}$]octane (**7a**) (11%), 5-*exo*-bromo-3-*exo*-bromomethyltricyclo[2.2.1.$0^{2,6}$]-heptane (**5a**) (11%), 6-*exo*-bromo-4-*exo*-methoxytricyclo[3.2.1.$0^{2,7}$]octane (**7b**) (39%) and 5-*exo*-bromo-3-*exo*-methoxymethyltricyclo[2.2.1.$0^{2,6}$]-heptane (**5b**) (29%). Separation was effected by radial chromatography (SiO_2, petroleum ether). The spectral data for 4-*exo*-6-*exo*-dibromotricyclo[2.1.0.$0^{2,7}$]octane (**7a**) and 5-*exo*-bromo-3-*exo*-bromomethyltricyclo-[2.2.1.$0^{2,6}$]heptane (**5a**) are identical to those reported for the reaction of *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**1**) with bromine in CCl_4 previously. **6-*exo*-Bromo-4-*exo*-methoxytricyclo[3.2.1.$0^{2,7}$]octane (7b)**: ^{1}H NMR δ_H ($CDCl_3$) 4.22 (s), $W_{h/2}$ = 3 Hz, H6*endo*; 3.27 (m), H4; 3.23, OMe; 2.44 (t), $^3J_{5,8}$ = $^3J_{5,4}$ = 3.2 Hz, H5; 2.15 (m), $^2J_{3endo,3exo}$ = 14.9 Hz, $^3J_{3endo,2}$ = 3.5 Hz, $^3J_{3endo,4}$ = 9.5 Hz, H3*endo*; 1.95, H8*anti*,H8*syn*; 1.77 (t of t), $^3J_{7,1}$ 7.5 Hz, $^3J_{7,2}$ 6.8 Hz, $^4J_{7,5}$ = $^4J_{7,8syn}$ 1.1 Hz, H7; 1.67 (m), $^2J_{3exo,3endo}$ 14.7 Hz, $^3J_{3exo,2}$ 2.1 Hz, $^3J_{3exo,4}$ 4.8 Hz, H3*exo*; 1.69 (s), $W_{h/2}$ = 14 Hz, H1; 0.95 (m), $^3J_{2,1}$ = $^3J_{2,7}$ 7.5 Hz, $^3J_{2,3exo}$ = 2.1 Hz, $^3J_{2,3endo}$ = 3.5 Hz, H2. ^{13}C NMR δ_C ($CDCl_3$) 77.5, C4; 56.3, C6; 55.8, OMe; 44.5, C5; 25.7, C7; 25.0, C3; 21.0, C8; 18.1, C1; 16.1, C2. MS: $C_9H_{13}OBr$ requires $M^{+\cdot}$ 216.0150; Found $M^{+\cdot}$ 216.0149. **5-*exo*-Bromo-3-*exo*-methoxymethyltricyclo[2.2.1.$0^{2,6}$]heptane (5b)**: ^{1}H NMR δ_H ($CDCl_3$) 3.95 (s), $W_{h/2}$ = 3.3 Hz, H5; 3.32, OMe; 3.26 (d of d), $^2J_{8a,8b}$ = 11.7 Hz, $^3J_{8a,3}$ = 8.6 Hz, H8a; 3.21 (d of d), $^2J_{8b,8a}$ = 11.7 Hz, $^3J_{8b,3}$ = 9.5 Hz, H8b; 2.13 (s), $W_{h/2}$ = 5 Hz, H4; 1.95 (d of t), $^2J_{7anti,7syn}$ = 11.5 Hz, $^4J_{7a,3}$ = $^4J_{7anti,4}$ 1.5 Hz, H7a; 1.92 (t), $^3J_{3,8a}$ = 8.6 Hz, $^3J_{3,8b}$ = 9.5 Hz, H3; 1.55 (t), $^3J_{6,1}$ = $^3J_{6,2}$ 5.3 Hz, H6; 1.53 (d), $^2J_{7syn,7anti}$ = 11.6 Hz, H7s; 1.38 (t), $^3J_{1,2}$ = $^3J_{1,6}$ 5.0 Hz, H1; 1.19 (t), $^3J_{2,1}$ = $^3J_{2,6}$ 5.2 Hz, H2. ^{13}C NMR δ_C ($CDCl_3$) 72.4, C8; 59.0, OMe; 57.0, C5; 43.3, C3; 39.2, C4; 27.3, C7; 19.6, C6; 16.7, C2; 11.7, Cl. MS: $C_9H_{13}OBr$ requires $M^{+\cdot}$ 216.0150; Found $M^{+\cdot}$ 216.0146.

Reaction of endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (2) *with bromine in CCl_4 To a solution of *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**2**) (83 mg) in CCl_4 (15 ml) was added with stirring bromine in CCl_4 (122 mg, 0.97 molar equivalent). After 2 minutes the solvent was removed under reduced pressure to yield a yellowish oil (183 mg, 88%). Glc analysis showed five products, shown to be 5-*exo*-bromo-3-*endo*-bromomethyltricyclo[2.2.1.$0^{2,6}$]heptane (**20a**) (59%), 6-*exo*-8-*anti*-dibromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**21a**) (22%) and 3 unknown compounds (5%, 6% and 7%). Separation was achieved by careful radial chromatography (SiO_2, pet. ether). **5-*exo*-Bromo-3-*endo*-bromomethyltricyclo[2.2.1.$0^{2,6}$]-heptane (20a)**: ^{1}H NMR δ_H ($CDCl_3$) 4.04 (s), $W_{h/2}$ = 2.5 Hz, H5; 3.23 (d of d), $^2J_{8a,8b}$ = 10.2 Hz, $^3J_{8a,3}$ = 7.7 Hz, H8a; 3.12 (d of d), $^2J_{8a,8b}$ = 10.2 Hz, $^3J_{8b,3}$ = 8.7 Hz, H8b; 2.12-2.16, H4, H7a; 2.04 (t), $^3J_{3,8a}$ = 7.7 Hz, $^3J_{3,8b}$ = 8.7 Hz, H3; 1.62-1.53, H6, H1; 1.38 (d), $^2J_{7s,7a}$ = 10.8 Hz, H7s; 1.23 (t), $^3J_{2,1}$ = $^3J_{2,6}$ 5.0 Hz, H2. ^{13}C NMR δ_C ($CDCl_3$) 53.6, C5; 48.1, C3; 40.8, C4; 32.6, C7; 32.5, C8; 19.3, C2; 18.3, C6; 14.4, Cl. MS: $C_8H_{10}Br_2$ requires $M^{+\cdot}$ 263.9150; Found $M^{+\cdot}$ 263.9140. **6-*exo*-8-*anti*-Dibromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (21a)**: ^{1}H NMR δ_H ($CDCl_3$) 3.98 (m,), $^3J_{6endo,7endo}$ = 8.0 Hz, $^3J_{6endo,7exo}$ = 4.5 Hz, $^4J_{6endo,8}$ = 1.5 Hz, H6*endo*; 3.78 (m), $^3J_{8syn,1}$ = $^3J_{8syn,5}$ = $^4J_{8syn,6endo}$ = $^4J_{8syn,7endo}$ 1.6 Hz, H8*syn*; 2.79 (t), $^4J_{5,1}$ = $^4J_{5,2}$ 1.5 Hz, H5; 2.58 (m), $^2J_{7endo,7exo}$ 13.4 Hz, $^3J_{7exo,6endo}$ = 4.5 Hz, $^3J_{7exo,1}$ = 3.3 Hz, H7*exo*; 2.50 (s), $W_{h/2}$ = 8 Hz, H1; 2.33 (m), $^2J_{7endo,7exo}$ = 13.4 Hz, $^3J_{7endo,6endo}$ = 8.0 Hz, $^4J_{7endo,8syn}$ = 1.8 Hz, H7*endo*; 0.98 (m,), $^3J_{2,3endo}$ = $^3J_{2,4}$ 7.3 Hz, $^3J_{2,3exo}$ 3.3 Hz, $^4J_{2,5}$ 1.5 Hz, H2; 0.88 (t of d), $^3J_{4,3exo}$ 3.2 Hz, $^3J_{4,3endo}$ = $^3J_{4,2}$ 7.3 Hz, H4; 0.78 (m), $^2J_{3exo,3endo}$ 7.0 Hz, $^3J_{3exo,2}$ = $^3J_{3exo,4}$ =

3.2 Hz, H3*exo*; 0.27 (m), $^2J_{3endo,3exo}$ = 7.0 Hz, $^3J_{3endo,2}$ = 7.2 Hz, $^3J_{3endo,4}$ = 7.3 Hz, H3*endo*. ^{13}C NMR δ_C ($CDCl_3$) 48.7, C5; 47.9, C6; 47.7, C8; 44.4, Cl; 41.8, C7; 16.4, C4; 15.2, C2; 4.8, C3. MS.: $C_8H_{10}Br_2$ requires $M^{+\cdot}$ 263.9150; Found $M^{+\cdot}$ 263.9149.

Reaction of 2 with bromine in methanol To a stirred solution of *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**2**) (240 mg) in anhydrous methanol (15 ml) was added bromine (360 mg, 0.99 molar equivalent) in methanol (1 ml). After 2 minutes, CCl_4 (5 ml) was added, the mixture washed with water and the organic layer separated. The extracts were dried over $MgSO_4$ and the solvent removed under reduced pressure to give a clear, colourless oil (503 mg, 98%) shown to contain 5-*exo*-bromo-3-*endo*-bromomethyltricyclo[2.2.1.$0^{2,6}$]heptane (**20a**) (17%), 6-*exo*-8-*anti*-dibromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**21a**) (4%), 5-*exo*-bromo-3-*endo*-methoxymethyltricyclo[2.2.1.$0^{2,6}$]heptane (**20b**) (31%) and 8-*anti*-bromo-6-*exo*-methoxy-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**21b**) (37%). Separation was effected by radial chromatography (SiO_2, eluted first with petroleum ether to give the dibromides and then 5% ether/petroleum ether to give the bromo-methoxy compounds). The spectral data for 5-*exo*-bromo-3-*endo*-bromomethyltricyclo[2.2.1.$0^{2,6}$]heptane (**20a**) and 6-*exo*,8-*anti*-dibromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (**21a**) are identical to those reported for the reaction of *endo*-tricyclo[3.2.1.$0^{2,4}$]octane (**2**) with bromine in CCl_4 previously. **8-*anti*-Bromo-6-*exo*-methoxy-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane (21b)**: ^{1}H NMR δ_H ($CDCl_3$) 3.68 (s), $W_{h/2}$ = 5 Hz, H8s; 3.55 (m), $^3J_{6endo,7endo}$ = 6.4 Hz, $^3J_{6endo,7exo}$ = 3.7 Hz, $^4J_{6endo,8syn}$ = 1.6 Hz, H6; 3.33, OMe; 2.67 (s), $W_{h/2}$ = 5 Hz, H5; 2.42 (s), $W_{h/2}$ = 7 Hz, H1; 2.08 (m), $^2J_{7exo,7endo}$ 12.6 Hz, $^3J_{7exo,1}$ = $^3J_{7exo,6endo}$ = 3.7 Hz, H7*exo*; 1.98 (d of d), $^2J_{7endo,7exo}$ = 12.6 Hz, $^3J_{7endo,6endo}$ = 6.4 Hz, H7*endo*; 0.90 (m), $^3J_{2,5}$ 1.4 Hz, $^3J_{2,3exo}$ 3.2 Hz, $^3J_{2,3endo}$ = $^3J_{2,4}$ = 7.4 Hz, H2; 0.76 (d of t), $^2J_{3exo,3endo}$ = 7.2 Hz, $^3J_{3exo,4}$ = $^3J_{3exo,2}$ = 3.2 Hz, H3*exo*; 0.62 (t of d), $^3J_{4,2}$ = $^3J_{4,3endo}$ = 7.2 Hz, $^3J_{4,3exo}$ 3.2 Hz, H4; 0.25 (m), $^2J_{3endo,3exo}$ = $^3J_{3endo,2}$ = $^3J_{3endo,4}$ = 7.2 Hz, H3*endo*. ^{13}C NMR δ_C ($CDCl_3$) 84.9, C6; 56.8, OMe; 48.4, C8; 43.8, Cl; 42.3, C5; 38.4, C7; 16.1, C4; 14.0, C2; 5.3, C3. MS: $C_9H_{13}OBr$ requires $M^{+\cdot}$ 216.0150; Found $M^{+\cdot}$ 216.0146. **5-*exo*-Bromo-3-*endo*-methoxymethyltricyclo[2.2.1.$0^{2,6}$]heptane (20b)**: ^{1}H NMR δ_H ($CDCl_3$) 4.22 (s), $W_{h/2}$ = 4 Hz, H5; 3.32, OMe; 3.29 (d of d), $^2J_{8a,8b}$ = 10.1 Hz, $^3J_{8b,3}$ = 8.1 Hz, H8a; 3.25 (d of d), $^2J_{8a,8b}$ = 10.1 Hz, $^3J_{8b,3}$ 9.6 Hz, H8b; 2.15-2.10, H7a, H4; 1.96 (t), $^3J_{8b,3}$ = 8.1 Hz, $^3J_{8b,3}$ = 9.6 Hz, H3; 1.52 (t), $^3J_{6,1}$ = $^3J_{6,2}$ = 5.2 Hz, H6; 1.44 (t), $^3J_{1,2}$ = $^3J_{1,6}$ = 5.0 Hz, H1; 1.42 (d), $^2J_{7a,7s}$ 10.8 Hz, H7s; 1.20 (t), $^3J_{2,1}$ = $^3J_{2,6}$ 5.1 Hz, H2. ^{13}C NMR δ_C ($CDCl_3$) 72.3, C8; 59.0, OMe; 55.4, C5; 45.3, C3; 39.1, C4; 32.5, C7; 18.4, C6; 17.0, C2; 13.1, C1. MS: $C_9H_{13}OBr$ requires $M^{+\cdot}$ 216.0150; Found $M^{+\cdot}$ 216.0146.

ACKNOWLEDGEMENTS: We thank the New Zealand Lottery Board for financial support of this study. With this paper we acknowledge the 65th birthday of Professor Dr Richard Neidlein.

REFERENCES AND FOOTNOTES

1 (a) Coxon, J. M.; Steel, P. J.; Whittington, B. I. *J. Org. Chem.* **1989**, *54*, 1383. (b) Coxon, J. M.; Steel, P. J.; Whittington, B. I. *J. Org. Chem.* **1989**, *54*, 3702. (c) Coxon, J. M.; Steel, P. J.; Whittington, B. I. *J. Org. Chem.* **1990**, *55*, 4136. (d) Coxon, J. M.; Steel, P. J.; Whittington, B. I.; Battiste, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 2988. Battiste, M.A.; Coxon, J.M. In *The Chemistry of the Cyclopropyl Group*, Rappoport. Z., Ed.; Wiley and Sons, **1987**, Chapter 6. Burritt, A; Coxon,

J.M.; Steel, P.J. In *Trends in Chemistry*, Research Trends, Council of Scientific Research Integration, India; 1993, 4, p517-534.

2 Crabtree, R.H. *Chem. Rev.* **1985**, *85*, 245. Lambert, J.B.; Chelius, E.C. *J. Organomet. Chem.* **1989**, *279*, 187.

3 Liu, H-W.; Walsh, C.T. In *The Chemistry of the Cyclopropyl Group*, Rappoport, Z., Ed.; Wiley and Sons, **1987**, Chapter 16, p 959.

4 Burritt, A; Coxon, J.M.; Steel, P.J.; Whittington, B.I. *J. Org. Chem.* 1995 In Press.

5 Lambert, J. B.; Chelius, E. C.; Schultz, Jr., W. J.; Carpenter, N. E. *J. Am. Chem. Soc.* **1990**, *112*, 3156. See also Lambert, J. B.; Schultz, W.J.; Mueller, P.H.; Kobayashir, K. *J. Am. Chem. Soc.* **1984**, *106*, 792. See also Battiste, M.A.; Coxon, J.M. *Tetrahedron Lett.* **1986**, *27*, 517.

6 <1.0 mole equivalent of bromine was used in order to minimise the risk of forming tetrabromo derivatives.

7 The presence of an *exo* cyclopropyl group follows by comparison of the chemical shifts (^{1}H and ^{13}C), and H-H coupling constants, with those of *exo*-tricyclo[3.2.1.0^{2,4}]octane.[1a]

8 This is similar to that observed for the analogous 6-*endo*-7-*exo*-dibromo-3,3-diphenyl-*exo*-tricyclo[3.2.1.0^{2,4}]octane the two CHBr peaks appearing as triplets (J = 3.0 Hz) at 4.37 ppm and 3.95 ppm. (see reference 26). The relevant proton-proton couplings for (**4**) are as follows: $^2J_{3exo,3endo}$ 6.3 Hz, $^3J_{3exo,4}$ 3.2 Hz, $^3J_{3endo,2} = {}^3J_{3endo,4}$ 7.1 Hz. Similarly, for *exo*-tricyclo[3.2.1.0^{2,4}]octane, H3*exo* at 0.28 ppm and H3*endo* at -0.11 ppm exhibit connectivity with C3 at 1.0 ppm, with coupling between H3*exo* and H3*endo* (6.0 Hz), H3*exo* and H2 (3.1 Hz), H3*exo* and H4 (3.1 Hz), H3*endo* and H2 (7.0 Hz) and H3*endo* and H4 (7.0 Hz).[1a]

9 This is similar to that observed for 6-*exo*-7-*exo*-dibromo-3,3-diphenyl-*exo*-tricyclo[3.2.1.0^{2,4}]octane[26] H6*endo* (H7*endo*) appearing as a doublet (J 2 Hz) at 4.10 ppm.

10 Similar to that observed for 6-*exo*-methoxy-2-methyltricyclo[3.2.1.0^{2,7}]octane. Burritt, A. PhD thesis, University of Canterbury, **1993**.

11 $^3J_{3exo,4exo} = {}^3J_{3endo,4endo}$ 11.0 Hz, $^3J_{3endo,4exo} = {}^3J_{3exo,4endo}$ 4.5 Hz. Bohlmann, F.; Rotard, W. *Liebigs Ann.* **1982**, 1220.

12 Evidence for the presence of the cyclopropyl group is found in the coupling between the cyclopropyl protons, in particular the couplings of C2-H ($^3J_{2,1} = {}^3J_{2,7}$ 7.0 Hz, $^3J_{2,3endo}$ 3.4 Hz, $^3J_{2,3exo}$ 1.9 Hz) and H7 ($^3J_{7,1} = {}^3J_{7,2}$ 6.6 Hz, $^4J_{7,5} = {}^4J_{7,8s}$ 1.3 Hz). The connectivity observed between H1, 1.67 ppm (C1, 18.0 ppm); H2, 1.00 ppm (C2, 18.4 ppm) and H7, 1.85 ppm (C7, 25.3 ppm), and in particular, the appearance of C1, C2 and C7 as methine carbons in an APT spectrum is consistent with the structure of **7a**.

13 A heteronuclear correlation spectrum identified connectivities between H5, 3.96 ppm (C5, 55.9 ppm) and H8a, 3.28 ppm and H8b, 3.18 ppm (C8, 32.4 ppm).

14 Japenga, J; Klumpp, G.W; Stapersma, J. *Tetrahedron.* **1977**, *33*, 2847.

15 Separation was achieved by radial chromatography.

16 The stereochemistry of C5-H in **5b** as *endo* follows from the appearance of a singlet in the ^{1}H NMR at 3.95 ppm. The changes in carbon and proton chemical shifts are consistent with the presence of a methoxy group at C8.

17 The magnitude of such a shift is dependent upon the proximity of the proton (carbon) nucleus to the methoxy group.

18 Roberts, I.; Kimball, G.E. *J. Am. Chem. Soc.* **1937**, *59*, 947.

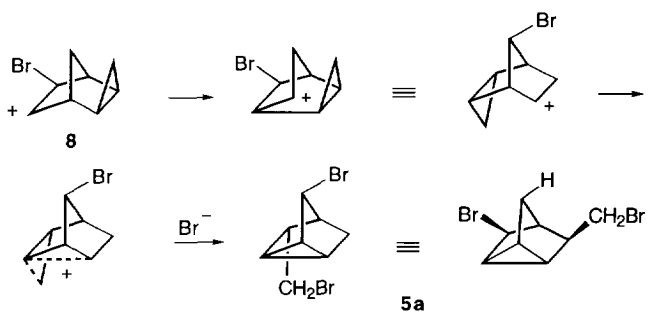
19 Slebocka-Tilk, H.; Ball, R.G.; Brown, R.S. *J. Am. Chem. Soc.* **1985**, *107*, 4504.

20 Galland, B.; Evleth, E. M.; Ruasse, M.-F. *J. Chem. Soc., Chem. Commun.* **1990**, 898.

21 Ab initio calculations suggest a shallow minimum corresponding to an open $C_2H_4Br^+$ cation. The shallow minimum has been suggested to result from incomplete geometry optimisation. Poirier, R. A.; Demaré, G. R.; Yates, K.; Csizmadia, I. G. *J. Mol. Struct. (THEOCHEM)* **1983**, *94*, 137. Poirier, R. A.; Mezey, P. G.; Yates, K.; Csizmadia, I. G. *J. Mol. Struct. (THEOCHEM)* **1981**, *85*, 153. Hamilton, T.P.; Schaefer, H.F. *J. Am. Chem. Soc.* **1990**, *112*, 8260.

22 Although the cations have been described as 'open' they do show some bridging of the bromine atom.

23 **5a** could be formed by Wagner Meerwein rearrangement followed by participation of the ensuing C1 cation with the *endo* C2C3 cyclopropyl bond. This mechanism, though more complex, cannot be excluded.



24 Haywood-Farmer, J. *Chem. Rev.* **1974**, *74*, 315 and references therein.

25 Traylor, T.G. *Acc. Chem. Res.* **1969**, *2*, 152.

26 Wilt, J; Malloy, T.P. *J. Org. Chem.* **1973**, *38*, 277

27 CCl_4 is considered a reasonable radical scavenger. Stirling, C.J.M. *Radicals in Organic Chemistry*, Oldbourne; London, **1965**, chapter 6.

28 The Br-Br bond is weaker than the Cl-C bond of CCl_4 and more susceptible to radical attack. Any alkyl radical generated from **1** or **2** would be expected to be sufficiently reactive to react on its first collision.

29 Hoz, S.; Livneh, M.; Cohen, D. *J. Am. Chem. Soc.* **1982**, *109*, 5149. Roth, H.D.; Schilling, M.L.; Gassman, P.G.; Smith, J.L. *J. Am. Chem. Soc.* **1984**, *106*, 2711.

30 This follows from a comparison with the reported ^{1}H NMR spectra of 5-*exo*-acetoxy-3-*endo*-methyltricyclo[2.2.1.$0^{2,6}$]heptane and 5-*endo*-acetoxy-3-*endo*-methyltricyclo[2.2.1.$0^{2,6}$]heptane, H5 in the former appearing as a broad singlet, while H5 in the latter appears as a broad triplet. Dell, A.; Johnson, B.L. *Aust. J. Chem.* **1978**, *32*, 2215.

31 H3*endo* 0.27 ppm, H3*exo* 0.78 ppm, H2 0.98 ppm, H4 0.88 ppm, $^2J_{3endo,3exo}$ 7.0 Hz, $^3J_{3endo,2} = {}^3J_{2,4}$ 7.2 Hz, $^3J_{3endo,4}$ 7.3 Hz, $^3J_{3exo,2} = {}^3J_{3exo,2} = {}^3J_{3exo,4}$ 3.2 Hz.

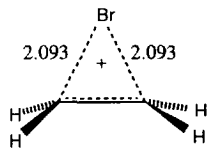
32 A heteronuclear shift correlation spectrum identified the proton-carbon one bond connectivities.

33 Adam, W.; Carballeira, N.; Peters, E.; Peters K.; Schnering, H.v. *J. Am. Chem. Soc.* **1983**, *105*, 5132.

34 Henshaw, B.C.; Rome, D.W.; Johnson, B.L. *Tetrahedron Lett.* **1968**, 6049 and *Tetrahedron* **1971**, *27*, 2255.

35 The corresponding angle defined by the plane of the bromonium ion and H-C6-C7-H decreases (**23** 97.7°; **11** 98.0°; **14**, 96.7°; **26**, 93.1°).

36



AM1 calculated bromonium ion formed from addition of Br^+ to ethylene.[20]

37 Kinns, M.; Sanders, J. K. M. *J. Magn. Reson.* **1984**, *56*, 518.

(*Received in UK* 18 *May* 1995; *accepted* 26 *May* 1995)