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ORBITAL CONTROL OF STEREOCHEMISTRY IN ACID-CATALYSED ADDITION REACTIONS OF *ENDO*-TRICYCLO[3.2.1.$0^{2,4}$]OCT-6-ENE†

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Abstract—The reaction of *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene **1** with methanol in the presence of catalytic amounts of toluene-p-sulphonic acid has been shown to give 2-*exo*- and *endo*-methoxybicyclo[3.2.1]oct-3-ene (**2c**) and (**2d**) and 2-*endo*-methoxybicyclo[3.2.1]oct-6-ene (**13**). The formation of 2-*exo*-methoxybicyclo[3.2.1]oct-3-ene (**2c**), the major product of reaction, has been probed by deuterium labelling experiments and a series of 6-*exo*-7-*exo*-dideuterobicyclo[3.2.1]oct-3-enes synthesised for ^{2}H, ^{1}H and ^{13}C NMR spectral analysis in order unambiguously to determine the stereochemistry of proton attack on *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (**1**). The formation of 2-*exo*-methoxybicyclo[3.2.1]oct-3-ene (**2c**) has been determined to involve corner protonation of the cyclopropyl moiety and skeletal rearrangement to an allylic cation with a small but measurable memory effect.

Some years ago we reported[1] the facile reaction of *endo* - tricyclo[3.2.1.$0^{2,4}$]oct - 6 - ene (**1**) with acetic acid to give a mixture (81:19) of *exo*- and *endo* - bicyclo[3.2.1]oct - 3 - en - 2 - yl acetates (**2a**) and (**2b**). The orbital geometry of alkene (**1**) is distinct (Fig. 1) with the strained C2–C4 bond in close parallel with the C1–C8 and C5–C8 bridgehead bonds. A feature of this topology is reflected in the facile expulsion[2] of carbon monoxide from *endo*-tricyclo[3.2.1.$0^{2,4}$]octan - 8 - one (**3**) and fragmentation of the ketone on reaction[3] with acid and water to 4-cycloheptene carboxylic acid (**4**). We now report a detailed study of the acid catalysed reactions of *endo* - tricyclo[3.2.1.$0^{2,4}$]oct - 6 - ene (**1**) utilising ^{2}H and high field NMR techniques. The reaction of this alkene with acetic acid suffers the disadvantage that any product allylic acetate (**2a**) or (**2b**) would undergo isomerisation[4] under the conditions necessary to cause rupture of the cyclopropyl C2–C4 σ-bond with concomitant loss of mechanistic information. The reaction of *endo* - tricyclo[3.2.1.$0^{2,4}$]oct - 6 - ene with methanol (D_1), in the presence of catalylic quantities of *p*-toluene sulphonic acid was studied since the expected allylic ether products of reaction would be stable under the reaction conditions. The study was designed to determine the importance or otherwise of a bicyclo[3.2.1]hept - 3 - en - 2 - yl cation in the reaction and to establish the stereochemistry of proton (deuteron) attack.

RESULTS AND DISCUSSION

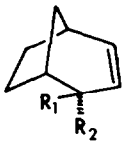
Corner protonated cyclopropanes have been invoked to rationalise hydrogen and carbon scrambling in carbocations.[5,6]

For example the isopropyl cation has been shown to rearrange by mechanisms (i) and (ii)[7] involving a "corner protonated cyclopropane" with proton exchange being only slightly faster than carbon exchange. The relative energy of "corner" (**5**) and "edge" (**6**) protonated cyclopropane and the involvement of protonated cyclopropanes in carbocation rearrangement reactions (iii) has been the subject of considerable debate and study.[6-8] A number of these studies have resulted in conflicting conclusions. Saunders *et al.*[7] suggested that the edge protonated structure (**6**) is at least a few kcal/mol less stable than corner protonated cyclopropane (**5**) and the calculations of Schleyer *et al.*[9] confirmed this view. The question of whether the methyl group in the corner protonated species is freely rotating is important and has been studied by MO calculations which suggest nearly free rotation. *Ab initio* calculations[10] including electron correlation effects while confirming the isopropyl $C_3H_7^+$ isomer (**7**) as the most stable isomer, 16.5 kcal mol^{-1} more stable than the n-propyl cation (**8**), find edge-protonated cyclopropane (**6**) more stable than corner protonated cyclopropane (**5**) by 5 kcal mol^{-1} and both more stable than the n-propyl cation (**8**). MINDO/3 calculations[11] also predict the most stable cyclic form to be the edge-protonated isomer (**6**) and derive a heat of formation value in close agreement with experiment. Experimental measurements have not differentiated the relative energies of edge vs corner protonated cyclopropane but show that protonated cyclopropane should be 8 kcal mol^{-1} less stable than the isopropyl cation.[12,13]

The corner protonated species (**9**) has been at the centre of the non-classical norbornyl cation contro-

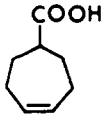
†For a preliminary report of this work see M. A. Battiste, J. M. Coxon, A. J. Jones, R. W. King, G. W. Simpson and P. J. Steel, *Tetrahedron Letters* **24**, 307 (1983).

(1)



(2)(a) R_1 = OAc, R_2 = H
(b) R_1 = H, R_2 = OAc
(c) R_1 = OMe, R_2 = H
(d) R_1 = H, R_2 = OMe
(e) R_1 = OH, R_2 = H
(f) R_1 = H, R_2 = OH

(3)



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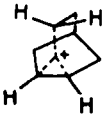

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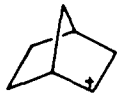

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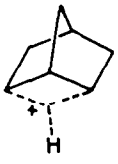

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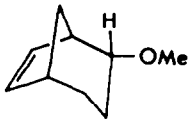

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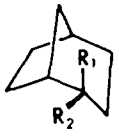


(14)(a) R_1 = OMe, R_2 = H
(b) R_1 = H, R_2 = OMe

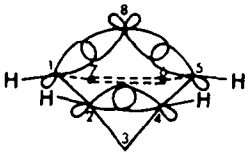
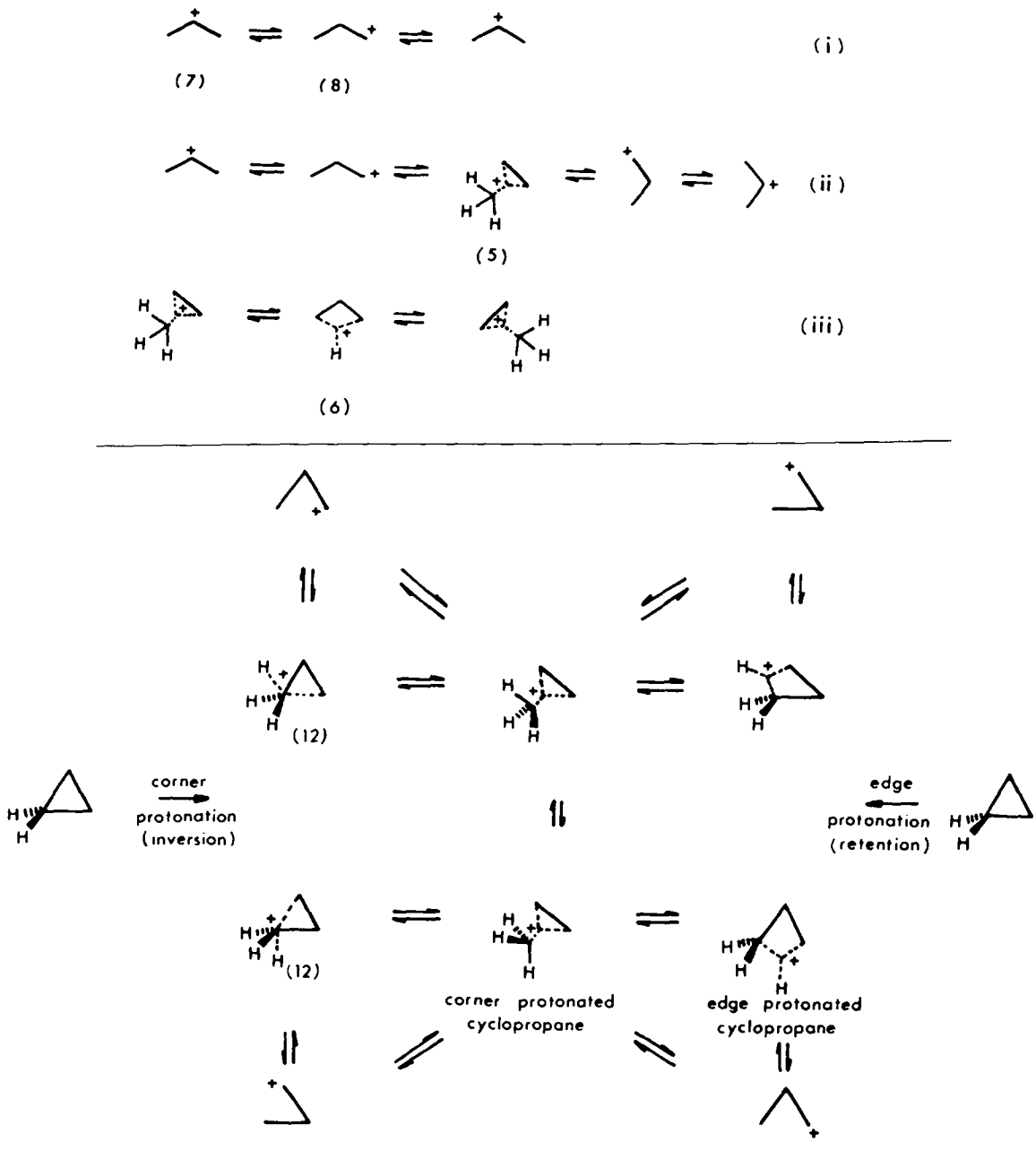


Fig. 1.

versy and its energy compared with the classical norbornyl cation (**10**) a matter of intense interest.[14] At low temperature NMR studies of the cation in super acid do not exclude the classical model (**10**) for the norbornyl cation but do place very restrictive limits on a barrier to interconversion of classical forms such that at 5°K the barrier can be no larger than 0.2 kcal mol^{-1}.[15] At higher temperatures H2, H1 and H6 hydrogen atoms and C2, C1 and C6 carbon atoms scramble. This scrambling, which involves 6,2-hydride and Wagner–Meerwein shifts, is analogous to that found in the cyclopropyl cation.[7] The experimentally observed activation energy 5.8 kcal mol^{-1} would represent the overall energy for these processes, the former involving edge protonated nortricyclene (**11**). The importance of these studies has overshadowed investigations of the stereochemistry of proton attack at cyclopropane.[5] This has led to some confusion between corner attack (attack with inversion of configuration) and corner protonated cyclopropane which is clarified in Scheme 1. This scheme also shows the importance of protonated cyclopropane in 1,2-methyl shifts. To date no calculations are known to us on the energy of the protonated cyclopropane structure (**12**) a species important for electrophilic cyclopropyl attack with inversion, the subject of the present study.

Addition reactions to cyclopropane derivatives have been reported which proceed with retention of both electrophile and nucleophile.[16] with inversion of electrophile and nucleophile[17] and with inversion of nucleophile with both retention and inversion of electrophile.[18] It has been argued that edge wise attack is the preferred mode of cyclopropane cleavage because the majority of polarizable electron density is located between the carbon atoms of the strained σ-bond.[19] It is however not possible to make generalisations concerning the stereochemistry of electrophilic attack at cyclopropane. The present study directs attention to this problem.

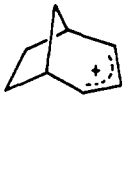
endo - Tricyclo[3.2.1.$0^{2,4}$]oct - 6 - ene[20] (**1**) can best be prepared by condensing cyclopropene at −78° in methylene chloride and adding approximately one molar equivalent of cyclopentadiene. The adduct was purified by spinning bond distillation. Reaction of *endo* - tricyclo[3.2.1.$0^{2,4}$]oct - 6 - ene (**1**) with acidified



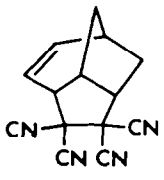
Scheme 1.

methanol (D_1) would be expected to cause rupture of the most substituted cyclopropyl σ-bond analogous to the reaction of the alkene (**1**) with acetic acid.† The mode and stereochemistry of proton (deuteron) attack, corner-inversion vs edge-retention, at the strained C2–C4 cyclopropyl σ-bond for this substrate can be distinguished if the stereochemistry of deuterium in the product can be determined unambiguously. Methanol was chosen as solvent and a suitable nucleophilic trap of carbocation intermediates since the ether products would be expected to be stable under the reaction conditions. Reaction of alkene (**1**) with methanol and catalytic quantities of toluene - p - sulphonic acid gave a mixture (86:2:12) of three products, 2 - *exo* - methoxybicyclo[3.2.1]oct - 3 - ene (**2c**), 2 - *endo* - methoxybicyclo[3.2.1]oct - 3 - ene (**2d**) and 2 - *endo*-methoxybicyclo[3.2.1]oct - 6 - ene (**13**). The major product (**2c**) was isolated by preparative GLC and its identity follows from the ^{1}H NMR spectrum which shows H2 (δ 3.26) coupled to H3 (δ 5.51) J 3.8 Hz and H1 J 3.0 Hz; H4 (δ 6.10) coupled to H3 J 9.5 Hz and H5 (δ 2.5) J 6.4 Hz. Hydrogenation gave methyl ether (**14a**) shown to be identical by GLC-MS, ^{1}H NMR and capillary GLC to an authentic sample prepared by hydrogenation of alcohol (**2e**)[4] followed by reaction with diazomethane in the presence of BF_3-diethyletherate. 2 - *endo* - Methoxybicyclo-

†We report experimental detail for this reaction not published in the original report.[1]



(15)



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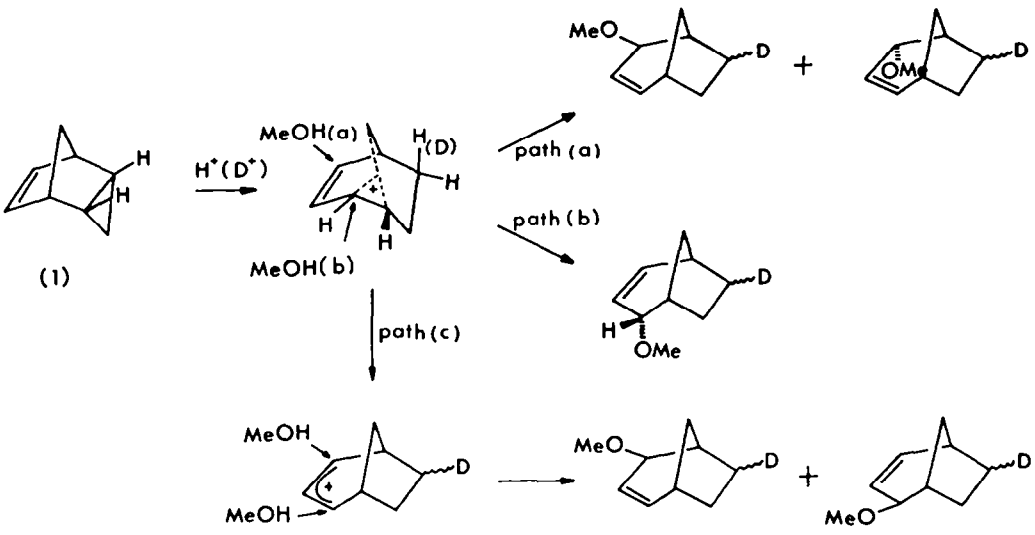
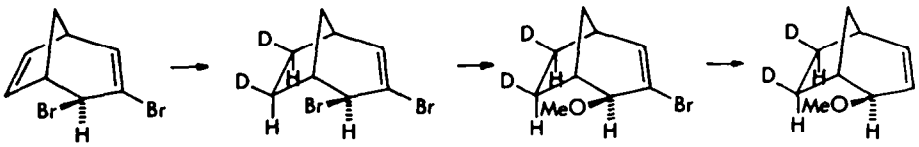


Scheme 2.

[3.2.1]oct - 6 - ene (**13**) was isolated by repeated preparative GLC and its identity established from the ^{1}H NMR spectrum which showed H2 (δ 3.26) coupled to H1 (δ 2.84) J 3.0 Hz which is deshielded by the double bond, and to $(H3)_2$ J 4.0, 8.0 Hz. The magnitude of the larger coupling to an adjacent H3 establishes the configuration of H2 as pseudo axial. H1 and H5 are coupled to H8*anti* (J 6 Hz and J 5 Hz respectively) and the apparent absence of coupling to H8*syn* is consistent with the geometry of the [3.2.1] skeleton. The configuration at C2 was further confirmed by hydrogenation to 2 - *endo* - methoxybicyclo[3.2.1]octane (**14b**) identical by GLC capillary column analysis to an authentic sample. The minor reaction product, 2 - *endo* - methoxybicyclo-[3.2.1]oct - 3 - ene (**2d**) was isolated by preparative GLC free of alkene (**13**) but contaminated with the *exo*-methoxyalkene (**2c**). Capillary column GLC analysis showed the product had the same retention time as an authentic sample and hydrogenation of the sample free of alkene (**13**) gave a product enriched in methoxy-ether (**14b**).

The reaction of alkene (**1**) with methanol – toluene-p-sulphonic acid parallels the reaction with acetic acid except that methoxy-alkene (**13**) was isolated and the proportion of *endo*-substituted alkene (**2d**) was less than *endo*-acetate (**2b**) produced in the acetic acid reaction. The formation of methoxy-alkene (**13**) involves attack of the nucleophile at the corner of the cyclopropane moiety and inversion of configuration and results from trapping the reaction in competition with rearrangement of C8 from C1 to C2. When cyclopropyl rupture is effected with acetic acid any primary product acetates (**2a**) or (**2b**) would isomerise *via* the allylic cation (**15**) to the thermodynamic equilibrium mixture (81:19) of allylic acetates[4] a reaction course not available to the methoxy-alkenes (**2c**) and (**2d**). If attack of the nucleophile (Scheme 2) occurs in concert with migration of C8 from C1 to C2 attack at C1 (path (b)) would give *endo*-product and attack at C6 predominantly *exo*-product (path (a)). Failure to detect significant quantities of *endo* product (**2d**) (2%) requires either that attack at C1 with inversion does not compete with attack at C6 or alternatively that reaction with the nucleophile occurs after an allylic cation is formed (path (c)), attack occurring almost exclusively from the *exo*-face. The predominant formation of *exo*-methoxyalkene (**2c**) suggests the intermediacy of an allylic cation (**15**) since solvolyses of *exo* - bicyclo[3.2.1]oct - 3 - en - 2 - yl *p*-nitrobenzoate, a reaction known to proceed *via* the allylic cation (**15**) results in 99.5% *exo*-alcohol formation.[4] These mechanistic alternatives can be differentiated if the reaction is effected with methanol (D_1) since the position of deuterium in the product can be used to distinguish nucleophilic attack at C1 and C6 which become C2 and C4 in the product methoxy-alkenes (Scheme 2). Furthermore the stereochemistry of the deuterium in the product(s) defines the stereochemistry of proton



(17) (18) (16)

Scheme 3.

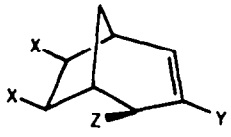
(deuteron) attack at C2 or C4 in the alkene (**1**). When the reaction was effected in methanol (D_1) in the presence of catalytic quantities of *p*-toluene sulphonic acid and the major methoxy-alkene isolated by preparative GLC a 90 MHz MNR spectrum showed a reduction in integral between δ 0.98 and *ca.* 1.4. The unresolved 90 MHz spectra mask the complexity of the assignment of the protons at C6 and C7 in the ^{1}H NMR spectrum. A ^{2}H NMR spectrum shows deuterium at δ 1.54 and δ 1.14 and the 270 MHz ^{1}H NMR spectrum showed resonances for C6 and C7 protons centred at δ 1.86, 1.58 and 1.20.

To establish unambiguously the assignment of the H6 and H7 signals an authentic sample of 6-*exo*, 7 - *exo* - dideuteromethoxybicyclo[3.2.1]hept - 3 - ene (**16**) was prepared (Scheme 3) by deuterogenation of 2 - *exo* - 3 - dibromobicyclo[3.2.1]octa - 3,6 - diene (**17**). The stereochemistry of deuterogenation was anticipated to be *exo* and this was established by the absence of H1, H7*exo* coupling in the 270 MHz ^{1}H NMR spectrum of dibromo alkene (**18**). This spectrum showed the 2H signal present at δ 1.75 (H6*exo*) in the undeuterated analogue to be reduced in intensity by 1H and the signal at δ 1.95 (H7*exo*) to be absent. The H7*endo* was observed at δ 1.5. The ^{2}H NMR spectrum showed signals at δ 1.94 (D7-*exo*) and 1.67 (D6*exo*). Replacement of the 2-bromo-atom with methoxide gave 3-bromo-6*exo*, 7 - *exo* - dideutero - 2 - *exo* - methoxybicyclo[3.2.1]oct - 3 - ene the ^{2}H NMR spectrum showed D7*exo*, δ 1.86, D6*exo*, δ 1.59 and ^{1}H NMR spectrum H7*endo* δ 1.65, H6*endo* δ 1.25. Reduction of the bromide gave 6 - *exo* - 7 - *exo* - dideutero - 2 - *exo* - methoxybicyclo [3.2.1]oct-3 - ene(**16**) with D7*exo* δ 1.80, D6*exo* δ 1.55 in the ^{2}H NMR spectrum and H7*endo* δ 1.55 and H6*endo* δ 1.22 in the 270 MHz ^{1}H NMR spectrum. The assignment of the chemical shift of the C6 and C7 protons of 2 - *exo* - methoxybicyclo[3.2.1]oct - 3 - ene; H6*exo* δ 1.55; H6*endo* δ 1.14; H7*exo*, δ 1.80; H7*endo*, δ 1.55; allows the position and stereochemistry of deuterium in the major product from the acid catalysed reaction of alkene (**1**) with methanol (D_1) to be determined. The ^{13}C NMR spectra of these compounds are reported in Table 1.

The major product from the reaction of alkene (**1**) is a mixture of 6 - *endo* - deutero - 2 - *exo* - methoxybicyclo[3.2.1]oct - 3 - ene (**19**) and 7 - *endo*-deutero - 2 - *exo* - methoxybicyclo[3.2.1]oct - 3 - ene (**20**). The signal at δ 1.14 in the ^{2}H NMR spectrum of the mixture is assigned as D6*endo* and the signal at δ 1.55 as the D7*endo*. The alternate assignment of this signal as D6-*exo* can be excluded on mechanistic grounds and from the fact that both C6 and C7 are reduced in intensity and coupled to deuterium in the ^{13}C NMR spectrum of the product.

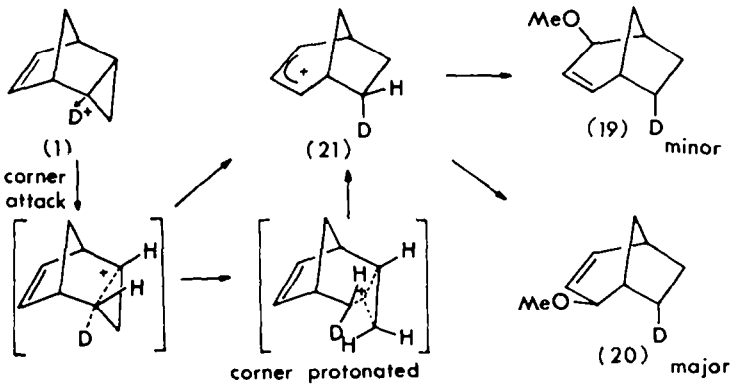
Formation of deutero alkenes (**19**) and (**20**) established that electrophilic attack in the acid catalysed opening of the cyclopropane moiety occurs with inversion of configuration. This corner attack of electrophile (Scheme 4) must not be confused with or

Table 1. ^{13}C NMR spectra of bicyclo[3.2.1]octenes

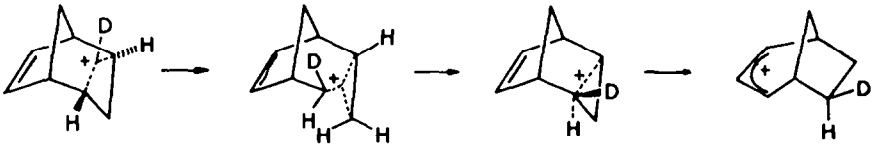


X	Y	Z	C1	C2	C3	C4	C5	C6	C7	C8	OMe
H	H	H[21]	33.6	37.5	123.8	134.7	35.6	35.5	30.6	35.5	
H	Br	Br	43.6	61.2	120.9	139.0	37.7	32.7	27.3	30.8	
D	Br	Br	43.6	61.2	120.9	139.0	37.6	32.3	26.9	30.8	
D	Br	OMe	(37.9)	86.8	121.2	138.9	(37.0)	30.7	23.9	30.7	58.0
H	H	OMe	(35.8)	81.3	123.1	138.5	36.2	31.3	24.9	31.4	56.3
D	H	OMe	(35.7)	81.1	123.1	138.4	(36.0)	31.0	24.4	31.2	56.3

All deuterated compounds showed C6 and C7 only as triplets, J 20Hz.



Scheme 4.



Scheme 5.

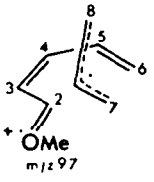


Fig. 2.

regarded to require the intermediacy of a corner protonated cyclopropane. A corner protonated cyclopropane would involve weakening of both the C2-C4 and C2-C3 σ-bonds with charge development at both C3, a primary carbon, and C4 a secondary carbon.

Integration of the ^2H NMR spectrum indicates a slight bias (*ca.* 1.1:1) for deuterium at C7 (**20**) vs C6 (**19**). A similar bias can be inferred from mass spectral studies. The mass spectrum of the undeuterated methoxy olefin (2c) exhibits a base peak *m/z* 97 (metastable 68.18) corresponding to an ion fragment $C_6H_9O^+$ (Fig. 2). From the intensity of the mass spectrum signals for the $C_6H_9O^+$ and $C_6H_8DO^+$ for the deuterated sample assuming fragmentation occurs as in Fig. 2 the deuterium content at C7 and C6 was calculated as *ca.* 1.1:1. For the reaction to involve an allylic cation (**21**) equal quantities of (**19**) and (**20**) would be formed. The small memory effect in favour of methoxy-alkene (**20**) suggests that C4 of cation (**21**), from which C8 has migrated, is marginally hindered relative to C2.

The corner attack of electrophile in this study parallels the observed corner attack of tetracyanoethene on alkene (**1**) in formation of adduct (**22**)[22] and adduct (**23**)[23] from similar attack on 2 - methylbicyclo[3.2.1.$0^{2,4}$]oct - 6 - ene. The unique orbital geometry of the alkene skeleton (Fig. 1) precludes any generalisation concerning the stereochemistry of proton attack at cyclopropane. The stereochemistry of deuterium in the product alkenes (**19**) and (**20**) precludes edge attack on the C2–C3 bond of alkene (**1**) and reorganisation to the corner protonated species (Scheme 5) in the reaction since such a process would require *exo*-deuterium in the product. The stereochemistry and results of this study can be accounted for if the reaction proceeds as shown in Scheme 4. There is no need to include edge protonation of cyclopropane or a corner protonated cyclopropane intermediate. The reaction proceeds by electrophilic attack at the corner of the cyclopropane ring and involves the intermediacy of an allylic cation and a small memory effect.

EXPERIMENTAL

Infrared spectra were recorded on a Shimadzu IR27G spectrophotometer and ^1H NMR spectra on a Varian T60 or Varian CFT20 spectrometer for $CDCl_3$ solutions with $CHCl_3$ and Me_4Si as internal standards. ^{13}C NMR spectra were recorded on a Varian CFT20 spectrometer equipped with a Sykes Compucorder for $CDCl_3$ solutions with $CHCl_3$ and Me_4Si as internal standards. ^2H and highfield ^1H NMR spectra were recorded at the National NMR Centre at Canberra and extensive decoupling experiments support assignments. Mass spectra were recorded on AEI MS902 and MS30 spectrometers. Analytical GLC was performed on Varian Aerograph 1200 and 1400 instruments. An Aerograph Autoprep 705 was used for preparative scale separations. Microanalytical data for new compounds was obtained whenever the stability and availability of the compound allowed.

Reactions of endo - *tricyclo*[3.2.1.$0^{2,4}$]*oct* - 6 - *ene with acetic acid*

A soln of *endo* - tricyclo[3.2.1.$0^{2,4}$]oct - 6 - ene (**1**) (1 g) in acetic acid (10 ml) was kept at 80° for 3 days. The mixture was diluted with water and the product extracted with pentane and washed with aqueous sodium bicarbonate to

remove all traces of acetic acid. After removal of solvent by distillation through a Vigreux column the mixture was analysed by GLC (2.5% Carbowax 20M on Chromosorb G AW DMCS) which showed a major peak, which was subsequently shown to be a mixture (4:1) of allylic acetates (**2a**) and (**2b**) and two minor components (<2%) one eluting before and one after the major peak. Integration of H2's after lithium aluminium hydride reduction of the crude reaction product indicated a 79:21 ratio of *exo*- and *endo*-alcohols (**2e**) and (**2f**) and GLC analysis a 78:22 ratio.

The major reaction component *exo* - bicyclo[3.2.1]oct - 3-en - 2 - yl acetate (**2a**) was isolated by preparative GLC (10% SE30 on Chromosorb W 30–60 mesh). ^{1}H NMR δ_H 6.23, $J_{3,4}$ 9.5 Hz, $J_{4,5}$ 7 Hz, $J_{1,2}$ 1.2 Hz, H4; 5.51, $J_{3,4}$ 9.5 Hz, $J_{3,2}$ 4.0 Hz, $J_{3,5}$ 1.7 Hz, H3; 4.87, $J_{2,3}$ 4 Hz, $J_{2,8anti}$ 2.5 Hz, H2; 2.03, OAc as a mixture with the *endo*-isomer (**2b**). To a sample of crude reaction mixture (0.5 g) in ether (10 ml) was added lithium aluminium hydride (0.1 g) and the mixture stirred for 30 min. The excess lithium aluminium hydride was decomposed by addition of excess $NaSO_4$, $10H_2O$. The ethereal solution was shown by GLC to be a 78:22 mixture of *exo*- and *endo* - bicyclo[3.2.1]oct - 3 - en - 2 - ols (**2e**) and (**2f**). Sublimation of the reaction product gave *exo* - bicyclo[3.2.1]oct - 3 - en - 2 - ol[4] (**2e**), contaminated with a trace of the *endo*-alcohol (**2f**) as white needles, m.p. 88–89°, ^{1}H NMR δ_H 6.10, $J_{4,3}$ 9.5 Hz, $J_{4,5}$ 7.0 Hz, J 1.0 Hz, H4; 5.49 $J_{3,4}$ 9.5 Hz, $J_{3,2}$ 4.0 Hz, $J_{3,5}$ 1.5 Hz, H3; 3.77, $J_{2,3}$ 4 Hz, $J_{2,8anti}$ 2,5 Hz, H2. An authentic sample of the *endo*-alcohol was obtained in the following manner. To a mixture of *exo*- and *endo*-alcohol (**2e**) and (**2f**) (250 mg) was added a six mole excess of chromium trioxide in pyridine and the mixture stirred at 0° for 12 h. The reaction product was isolated with pentane and filtered through Al_2O_3 to give bicyclo[3.2.1]oct - 3 - en - 2 - one[4] as an oil ν_{max} 6.0 and 5.9$_{sh}$ μ. The ketone (100 mg) was reacted with lithium aluminium hydride (30 mg) in ether (10 ml) to give after decomposition of the excess lithium aluminium hydride with Na_2SO_4, $10H_2O$ a mixture (GLC 91:9) of *endo*- and *exo* - bicyclo[3.2.1]oct - 3 - en - 2 - ols (**2f**) and (**2e**). The *endo*-alcohol (**2f**) was obtained free of the *exo*-alcohol (**2c**)[4] by preparative GLC, m.p. 82–83°, ^{1}H NMR δ 5.97 $J_{4,3}$ 9.5 Hz, $J_{4,5}$ 6.0, $J_{4,6}$ 1.5 Hz, $J_{4,8anti}$ 1.5 Hz, H4; 5.33, $J_{3,4}$ 9.5 Hz, $J_{3,2}$ 2.0 Hz, $J_{3,5}$ 2.0 Hz, H3; 4.56, Wh/2 10 Hz, H_2. Acetylation of *endo*-alcohol (**2f**) (3 mg) with acetic anhydride-pyridine at room temperature for 12 h and isolation by means of pentane gave the *endo*-acetate (**2b**). This acetate had identical retention to GLC as the epimeric acetate (**2a**).

Isomerisation of endo - *bicyclo*[3.2.1]*oct* - 3 - *en* - 2 - *yl acetate* (**2b**)

(i) A soln of *endo* - bicyclo[3.2.1]oct - 3 - en - 2 - yl acetate (1 mg) (**2b**) in acetic acid was kept at 80° for 3 days. The product was isolated by means of ether and the product reacted with lithium aluminium hydride in ether to give a mixture (65:35 by GLC) of *exo*- and *endo*-alcohols (**2e**) and (**2f**).

(ii) *With toluene - p - sulphonic acid in methanol.* A soln of *endo* - tricyclo[3.2.1.0^{2,4}]oct - 6 - ene (**1**) (3.35 g) and toluene - p - sulphonic acid (100 mg) in methanol (30 ml) was kept at 20° for 5 days. The mixture was diluted with water and the product extracted with pentane. After removal of all traces of acid by washing with aqueous sodium bicarbonate the solvent was removed by distillation through a Vigreux column. Analysis by GLC showed the presence of three products (in order of elution 12:2:86) in addition to starting alkene (26%). In a separate experiment under the same reaction conditions, but adding o-xylene immediately prior to isolation the GLC analysis accounted for >90% material balance. The two major products of the reaction were separated by preparative GLC. The major product, 2-*exo* - methoxybicyclo[3.2.1]oct - 3 - ene, was isolated as an oil. ^{1}H NMR δ_H 6.1 $J_{4,3}$ 9.4 Hz, $J_{4,5}$ 6.6 Hz, $J_{4,2}$ *c.* 0.8 Hz H4; 5.55, $J_{3,4}$ 9.4 Hz, $J_{3,2}$ 4.0 Hz, $J_{3,5}$ 1.8 Hz, H3; 3.38, OMe; 3.28 $J_{2,3}$ 4 Hz, $J_{2,1}$ *c.* 2.5 H2. *m/z* 138 (29%), 97 (100). Careful and repeated preparative GLC afforded 2 - *endo* - methoxybicyclo[3.2.1]oct - 6 - ene (2 mg) as an oil, ^{1}H NMR δ_H 5.92, Wh/2 4 Hz, H6, H7; 3.34, OMe; 3.26, $J_{2,3ax}$ 8 Hz, $J_{2,1}$ 3 Hz, $J_{2,3eq}$ 4.5 Hz, H2; 2.84, $J_{1,8a}$ 6 Hz, J *c.* 0.5 Hz, H1; 2.53, $J_{5,8a}$ 5.2 Hz, $J_{5,4ax}$ 2.7 Hz, $J_{5,4eq}$ 2.7, H5; 2.05, $J_{8anti,1}$ 6.0 Hz, $J_{8anti,5}$ 5.2 Hz, $J_{8anti,8syn}$ 10.5 Hz, $J_{8anti,4eq}$ *c* 1.0 Hz, H8*anti*; 1.31, $J_{8syn,8anti}$ 10.5 Hz, $J_{8syn,1}$ *c.* OHz, $J_{8syn,5}$ *c.* OHz, $J_{8syn,6}$ < 1.0 Hz, $J_{8syn,7}$ < 1.0 Hz. *m/z* 138 (24), 106 (66), 91(46), 71 (100).

(iii) *With toluene - p - sulphonic acid in methanol* (D_1). A soln of *endo* - tricyclo[3.2.1.0^{2,4}]oct - 6 - ene (1.0 g) and toluene - p - sulphonic acid (30 mg) in methanol (D_1) (15 ml) was kept at 40° for 7 days. The product was obtained in the usual manner and preparative GLC gave a mixture of 6 - *endo* - deutero- and 7 - *endo* - deutero - 2 - *exo* - methoxybicyclo[3.2.1]oct - 3 - ene (**19**) and (**20**), ^{1}H NMR ($CDCl_3$) (270 MHz) δ_H 6.10, $J_{4,3}$ 9.45 Hz, $J_{4,5}$ 6.48 Hz, $J_{4,2}$ 1.08 Hz, $J_{4,8anti}$ 1.08 Hz, H4; 5.51, $J_{3,4}$ 9.7 Hz, $J_{3,2}$ 3.91 Hz, $J_{3,5}$ 1.75 Hz, H3; 3.38, OMe; 3.26, $J_{2,3}$ 3.8 Hz, $J_{2,1}$ 3.0 Hz, H2; 2.5, Wh/2 32 Hz, H1, H5; 1.86, Wh/2 32 Hz, H7*exo*; 1.73; $J_{8syn,8anti}$ 11.5, ^{4}J 1 Hz, H8*syn*; 1.58, Wh/2 22 Hz, H6*exo*, H7*endo*; 1.22, $J_{8anti,8syn}$ 11.5 Hz, H8*anti*; 1.20, Wh/2 16 Hz H6*endo*. ^{2}H NMR δ_D 1.54 D7*endo*; 1.14, D6*endo*. ^{13}C NMR δ_C 24.9(s), 24.6(t) J 20 Hz, C7; 31.3(s), 31.2(t) J 20 Hz, C6; 31.2, C8; 35.7, 36.0. C1, C5; 56.3, OMe; 81.2, C2; 123.1, C3; 138.4, C4. *m/z* 139 (70), 98 (95), 97 (100).

Preparation of 6exo,7exo - *dideutero* - 2 - exo - *methoxybicyclo*[3.2.1]*oct* - 3 - *ene*

A freshly prepared mixture containing 2 - *exo* - 3 - dibromobicyclo[3.2.1]octa - 3,6 - diene[24] (5 g) formed from reaction of norbornadiene, bromoform and potassium t-butoxide, was kept in a hydrogen atmosphere with Pd/C (0.5 g; 10%) at ambient temperature and pressure until one mole equivalent of hydrogen had been taken up. The product was distilled to give 2 - *exo* - 3 - dibromobicyclo[3.2.1]oct - 3 - ene (**3g**) as a colourless oil,[24] b.p. 110–112° at 4 mm Hg, ν_{max} (film) 2950, 2875, 1620 and 1450 cm^{-1}. ^{1}H NMR ($CDCl_3$) (270 MHz) δ_H 6.33, $J_{4,5}$ 7.03, ^{4}J 0.97 Hz, H4; 4.53, $J_{2,1}$ 2.8 Hz, H2; 2.86, Wh/2 20 Hz, H1; 2.63, Wh/2 20 Hz, H5; 2.21, $J_{8syn,8anti}$ 11.7 Hz, H8*syn*; 1.95, Wh/2 36 Hz, H7*exo*; 1.75, Wh/2 25 Hz, H6*exo*, H7*endo*; 1.50, Wh/2 34 Hz, H6*endo*, H8*anti*. *m/z* 269(2), 268(17), 267(16), 266(35), 265(23), 264(23), 263(3), 262(9), 188(7), 187(94), 186(17), 185(100), 184(4), 183(13), 161(1), 160(4), 159(55), 158(13), 157(60), 156(10). The above reaction was repeated on a freshly prepared mixture containing 2 - *exo*-3 - dibromobicyclo[3.2.1]octa - 3,6 - diene (**17**) (15 g) which was vigorously stirred with Pd/C (1.5 g; 10%) in a deuterium atmosphere at ambient temperature and pressure until ca. one mole equivalent of deuterium had been taken up (24 h). The product was distilled to give 6*exo* - 7 - *exo* - dideutero-2 - *exo* - 3 - dibromobicyclo[3.2.1]oct - 3 - ene (9 g), b.p. 110–115° at 4 mm Hg, ν_{max} (film) 2950, 2875, 2180 (C-Dstr), 1620, 1480 cm^{-1}. ^{1}H NMR ($CDCl_3$) (270 MHz) δ_H 6.34, $J_{4,5}$ 7.07, ^{4}J 0.97 Hz, H4; 4.53, $J_{2,1}$ 2.8 Hz, H2; 2.86, Wh/2 12 Hz, H1; 2.63, Wh/2 14 Hz, H5; 2.21, $J_{8syn,8anti}$ 11.7 Hz, H8*syn*; 1.75, Wh/2 17 Hz, H7*endo*; 1.5, Wh/2 22 Hz, H6*endo*. ^{2}H NMR ($CDCl_3$) δ_D 1.94, D7*exo*; 1.67, D6*exo*. ^{13}C NMR ($CDCl_3$) δ_C 26.7(t), J 20 Hz, C7; 30.8, C8; 32.3(t) J 20 Hz, C6; 37.6, C5; 43.6, C1; 61.2, C2; 120.9, C3; 139.1, C4. *m/z* 271(2), 270(11), 269(4), 268(23), 267(13), 266(13), 265(9), 264(3), 190(15), 189(95), 188(65), 187(100), 186(53). To a soln of 6 - *exo* - 7 - *exo* - dideutero - 2 - *exo* - 2,3 - dibromobicyclo[3.2.1]oct - 3 - ene (2 g) on dry methanol (25 ml) was added toluene - p - sulphonic acid (100 mg) and the mixture heated under reflux for 6 h and poured into a mixture of water (100 ml) and ether (200 ml). The aqueous layer was extracted several times with ether and the combined ether layers dried over magnesium sulphate. Removal of solvent gave 3 - bromo - 6 - *exo* - 7 - *exo* - dideutero - 2 - *exo* - methoxybicyclo[3.2.1]oct - 3 - ene as a dark coloured oil which was used directly for the preparation of 3 - bromo - 6 - *exo* - 7 - *exo* - dideutero - 2 - methoxybicyclo[3.2.1]oct - 3 - ene. A sample was purified by preparative GLC to give 3 - bromo - 6 - *exo* - dideutero -

2 - *exo* - methoxybicyclo[3.2.1]oct - 3 - ene as a colourless oil. Found: C, 49.5; H, 5.7. $C_9H_{11}BrD_2O$ requires C, 49.3; H, 6.0%. ν_{max} 2880, 2830, 2810, 2300 (C–D str), 1830, 1650, 1580, 1390, 1300, 1240, 1180, 1100, 890 cm^{-1}. ^1H NMR ($CDCl_3$) (270 MHz) δ_H 6.50 $J_{4,5}$ 7.1 Hz, H4; 3.49, OMe; 3.31 $J_{1,2}$ 2.9 Hz, H2; 2.64, Wh/2 12 Hz, H1; 2.55, $J_{5,6endo}$ 2.4, $J_{5,8anti}$ 7.2 Hz, H5; 1.80 $J_{8anti,8syn}$ 10.8 Hz, H8*syn*; 1.65, $J_{6endo,7endo}$ 7.2 Hz, H7*endo*; 1.25, Wh/2 17 Hz, H6*endo*, H8*anti*. ^2H NMR ($CDCl_3$) δ_D 1.86, D7*exo*; 1.59, D6*exo*. ^{13}C NMR ($CDCl_3$) δ_C 23.9(t) J 20 Hz, C7; 30.7(t) J 20 Hz, C6; 30.7, C8, 37.0, C1–C5; 58.0 OMe; 86.8, C2; 121.2, C3; 138.9, C4. *m/z* 220(25), 18(10), 140(5), 139(100), 138(17), 109(33), 107(19), 97(45). To a mixture of crude 3 - bromo - 6 - *exo* - 7 - *exo*-dideutero - 2 - *exo* - methoxybicyclo[3.2.1]oct - 3 - ene (600 mg) in ether (2 ml) and liquid ammonia (25 ml) was added sodium (150 mg) and the mixture stirred at room temperature for 5 min. The ammonia was allowed to evaporate and water carefully added. The mixture was extracted with ether and the solution dried over magnesium sulphate. The product mixture after removal of solvent was subjected to preparative GLC to give 3 - bromo - 6 - *exo* - 7 - *exo* - dideutero - 2 - *exo* - methoxy[3.2.1]oct - 3 - ene (145 mg) identical to the above sample and 6 - *exo* - 7 - *exo* - dideutero- 2 - *exo* - methoxybicyclo[3.2.1]oct - 3 - ene (**16**) (120 mg) as an oil. ^1H NMR ($CDCl_3$) (270 MHz), δ_H 6.10, $J_{4,3}$ 9.45 Hz, $J_{4,5}$ 6.48 Hz, $J_{4,2}$ 1.08 Hz, $J_{4,8anti}$ 1.08 Hz, H4; 5.51, $J_{3,4}$ 9.7 Hz, $J_{3,2}$ 3.91 Hz, $J_{3,5}$ 1.75 Hz, H3; 3.38, OMe; 3.26, $J_{2,3}$ 3.8, $J_{2,1}$ 3.0 Hz, H2; 2.50, Wh/2 27 Hz, H1, H5; 1.73, $J_{8syn,8anti}$ 11.5 Hz, ^4J 1 Hz, H8*syn*, 1.55, $J_{6endo,7endo}$ 8.98 and J 1.8 Hz, H7*endo*; 1.22 Wh/2 20 Hz, H6*endo*; 1.22, $J_{8anti,8syn}$ 11.5 Hz, H8a. ^2H NMR ($CDCl_3$) δ_D 1.80, D7*exo* and 1.55, D6*exo*; ^{13}C NMR $CDCl_3$ δ_C 24.4(t), J 20 Hz, C7; 31.0(t), J 20 Hz, C6; 31.2, C8; 35.7, 36.0, C1, C5; 56.3, OMe; 81.1, C2; 123.1 C3; 138.4, C4. *m/z* 141(3), 140(28), 139(16), 110(20), 109(14), 101(21), 98(100), 97(10), 82(26).

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