Some Stereocontrolled Ring-opening Reactions of 6-Substituted 2,3-Epoxybicyclo[3.2.0]heptanes

Roger F. Newton* and Derek P. Reynolds
Chemical Research Laboratories, Glaxo Group Research, Ware, Herts. SG12 0DJ
Paul B. Kay, Timothy W. Wallace, and Stanley M. Roberts
Department of Chemistry, Salford University, Salford M5 4WT
Robert C. Glen and Peter M. Murray-Rust *
Department of Chemistry, University of Stirling, Stirling FK9 4LA

The bicyclo[3.2.0]heptenes (7), (9), (10), (12), and (13) were prepared and treated with a brominating agent in an aqueous medium. The alkenes (9) and (10) gave only the bromohydrins (15) and (16), respectively. The bicycloalkenes (7), (12), and (13) gave mixtures of bromohydrins. The mixture obtained from compound (12) gave the epoxides (32) and (35) on treatment with base: similarly the bromohydrins obtained from the alkenes (7) and (13) were converted into the isomeric epoxide pairs (29)/(34), and (33)/(36), respectively. The epoxides (30) and (31) were furnished by base-treatment of the bromohydrins (15) and (16), respectively. The epoxides (29)—(33) were treated with lithium dibutyl cuprate. The epoxides (30) and (31) reacted with high selectivity to give the corresponding bicycloalkan-3-ols (19) and (20) almost exclusively. The epoxides (32) and (33) reacted non-selectively with this cuprate reagent. The parent epoxide (29) displayed an intermediate behaviour, giving a mixture of the alcohols (18) and (23) with the former compound predominating. These results are explained by assuming that a substituent at the 6-position in this ring-system exerts a perannular conformational control which affects the selectively of reaction of an alkene and epoxide unit at C-2 and also influences the conformation of 2,3-disubstituted derivatives.

A key reaction in an efficient route to prostaglandins E_2 and $F_2\alpha$ involved the opening of the epoxy-acetal (1) with the cuprate reagent (2) to give predominantly the alcohol (3) (84%).[1] The isomer (4) (16%) was removed by column chromatography. The acetal (1) reacted with lithium dibutyl cuprate to give the alcohols (5) and (6) in the ratio 4 : 1.

We reasoned that if the four-membered ring was responsible for the observed regioselectivity of the cuprate reactions,[2] then modification of the substitution pattern in this ring might lead to even greater selectivity. We report the results obtained on treating various bicyclo[3.2.0]heptane epoxides with lithium dibutyl cuprate.

Results

Bicyclo[3.2.0]hept-2-ene (7) [3] was converted into a mixture of bromohydrins using *N*-bromoacetamide (NBA) in an aqueous medium. The major product, the bromohydrin (14), could be isolated by chromatography. Treatment of the mixture with base gave the epoxides (29) and (34) in the ratio 95 : 5.

The bicycloheptanol (8) [4] was converted into the methyl ether (9) and the trityl ether (10). These ethers formed only the bromohydrins (15) and (16), respectively, when brominated with NBA (or *N*-bromosuccinimide, NBS) in aqueous acetone. The bicycloheptene (10) formed only the bromomethoxy-compound (28) when brominated using NBS in methanol. Each of the bromohydrins (15) and (16) was treated with potassium t-butoxide to furnish the required epoxides (30) and (31).

The alcohol (11) [4] was readily converted into the methyl ether (12). This compound reacted with NBA in aqueous acetone to produce a mixture of bromohydrins which was treated with potassium t-butoxide to give the *endo*-epoxide (32) and the *exo*-epoxide (35) in the ratio 17 : 3. The former epoxide is derived from 2(3)-*exo*-bromo-6-*exo*-methoxybicycloheptan-3(2)-*endo*-ols while the latter epoxide is derived from 2(3)-*endo*-bromo-6-*exo*-methoxybicycloheptan-3(2)-*exo*-ols. Thus, bromonium-ion formation from the alkene (12) is non-specific.

Similar treatment of the 6-*exo*-trityloxybicycloheptene (13) with NBS in aqueous acetone, isolation of the product bromohydrins, and dehydrobromination with base gave the epoxides (33) and (36) in the ratio 5 : 2. We assume that this ratio gives an approximate indication of the selectivity of bromonium-ion formation from the alkene (13). Chromatography of the mixture of bromohydrins gave the compound (17).

The epoxide (29) reacted with lithium dibutyl cuprate at low temperature to give the two alcohols (18) and (23) in the ratio 73 : 27 (65% yield). Our assignment of stereochemistry followed from the fact that the major component of this mixture was identical (g.l.c., m.s.) with the product obtained on Huang-Minlon-modified Wolff–Kishner reduction of the ketone (37).[2,5]

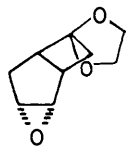
Lithium dibutyl cuprate attack on the 6-*endo*-alkoxyepoxides (30) and (31) was highly regioselective. Thus, the methoxyoxiran (30) gave mainly the alcohol (19) (70%): a small amount ($\leq 3\%$) of a second component [presumably the isomeric alcohol (24)] was observed by 400-MHz ^{1}H n.m.r. spectroscopy. The trityloxyoxiran (31) reacted with the cuprate reagent to give a mixture of the alcohols (20) (64.0%) and (25) (12.0%) which was separated by chromatography.

In direct contrast with the above results, the 6-*exo*-alkoxyepoxides (32) and (33) reacted non-selectively with lithium dibutyl cuprate: the *exo*-methoxy-compound (32) gave almost equal amounts of the alcohols (21) and (26) while the *exo*-trityloxy-compound (33) gave the alcohols (22) and (27) in the same ratio (55 : 45).

Thus the selectivity of bromonium-ion formation from a bicyclo[3.2.0]hept-2-ene depends on the orientation and the nature of the substituent at C-6. The selectivity of ring opening of the corresponding 2,3-*endo*-epoxybicyclo[3.2.0]heptane with lithium dibutyl cuprate varies similarly (Table).

Discussion

The above results can be rationalized if it is assumed that in the bicyclo[3.2.0]heptene system the four-membered ring is puckered [6] and a substituent at C-6 preferentially takes up



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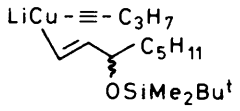

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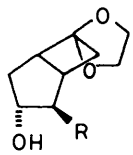
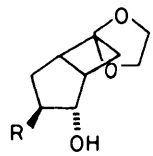
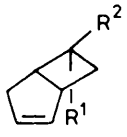
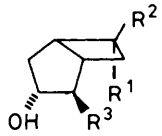


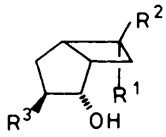


(3) R = CH=CHCHC$_5$H$_{11}$ (4)
OSiMe$_2$Bu^t

(5) R = C$_4$H$_9$ (6)



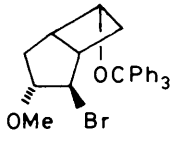




(7) R^1 = R^2 = H
(8) R^1 = OH, R^2 = H
(9) R^1 = OMe, R^2 = H
(10) R^1 = OCPh$_3$, R^2 = H
(11) R^1 = H, R^2 = OH
(12) R^1 = H, R^2 = OMe
(13) R^1 = H, R^2 = OCPh$_3$

(14) R^1 = R^2 = H, R^3 = Br
(15) R^1 = OMe, R^2 = H, R^3 = Br
(16) R^1 = OCPh$_3$, R^2 = H, R^3 = Br
(17) R^1 = H, R^2 = OCPh$_3$, R^3 = Br
(18), (23) R^1 = R^2 = H, R^3 = Bu
(19), (24) R^1 = OMe, R^2 = H, R^3 = Bu
(20), (25) R^1 = OCPh$_3$, R^2 = H, R^3 = Bu
(21), (26) R^1 = H, R^2 = OMe, R^3 = Bu
(22), (27) R^1 = H, R^2 = OCPh$_3$, R^3 = Bu

(23) - (27)



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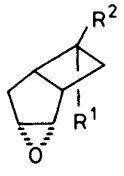
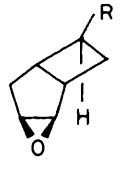
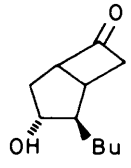


(29) R^1 = R^2 = H
(30) R^1 = OMe, R^2 = H
(31) R^1 = OCPh$_3$, R^2 = H
(32) R^1 = H, R^2 = OMe
(33) R^1 = H, R^2 = OCPh$_3$



(34) R = H
(35) R = OMe
(36) R = OCPh$_3$



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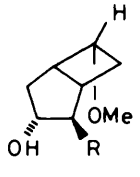
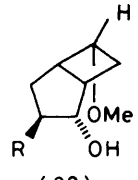
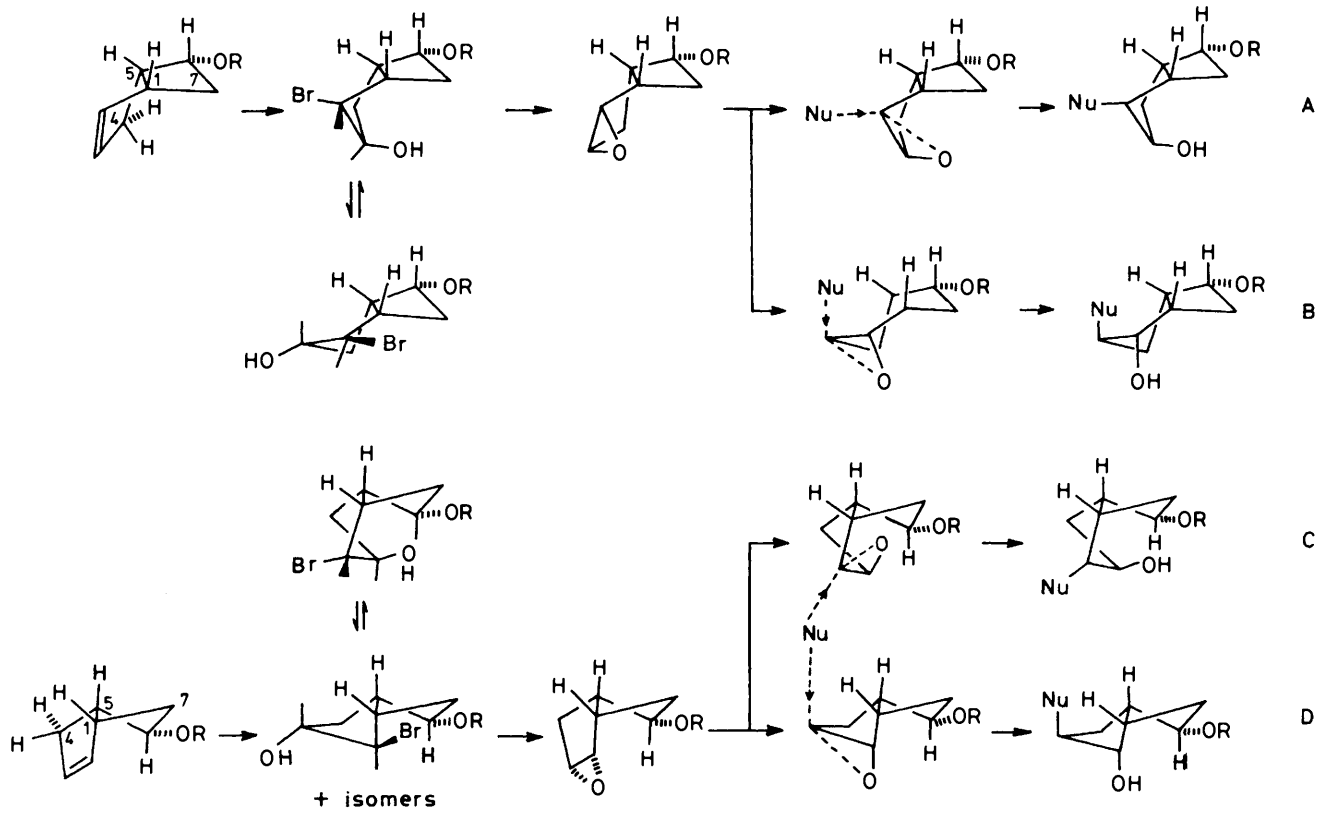




(38) R = CH=CHCHC$_5$H$_{11}$ (39)
OSiMe$_2$Bu^t

a pseudo-equatorial position. This sets a constraint on the flexibility of the four-membered ring and dictates the torsion angle between C-1 and C-5 (Figure).

The *endo*-alkoxybicycloheptenes (9) and (10) each gave only one bromohydrin (15) and (16), respectively, on bromination under aqueous conditions: no diastereoisomeric compounds were observed by ^{1}H n.m.r. spectroscopy or t.l.c. These bromohydrins can exist in two limiting conformations but that in which the five-membered ring has an *endo*-envelope form is much preferred (the required torsion angle about C-1–C-5 suggests strain in the *exo*-envelope form). Thus, for both compounds, ^{1}H n.m.r. spectroscopy clearly shows $J_{2,1} = J_{2,3} \leqslant 1$ Hz, indicating the *endo*-envelope form for the five-membered ring ($\omega_{2,1} = \omega_{2,3}$ *ca.* 90°) is preferred.[7] I.r. dilution studies on



Figure

Table. Bromonium-ion formation from bicyclo[3.2.0]heptenes substituted at C-6, and regioselectivity of cuprate attack on 2,3-*endo*-epoxybicyclo[3.2.0]heptanes substituted at C-6

6-Substituent	Ratio of products derived from *exo*- and *endo*-bromonium ions	Ratio of bicycloheptan-2-ol to bicycloheptan-3-ol obtained on reaction of lithium dibutyl cuprate with 2,3-epoxide
exo-Trityloxy (13)	5 : 2	45 : 55
exo-Methoxy (12)	85 : 15	45 : 55
None (7)	19 : 1	23 : 77
endo-Trityloxy (10)	>20 : 1	15 : 85
endo-Methoxy (9)	>20 : 1	3 : 97

the bromohydrin (16) show that intramolecular hydrogen bonding does exist between the 3-*endo*-hydroxy- and the 6-*endo*-trityloxy-group ($\nu_{max.}$ 3 425 cm^{-1}, independent of concentration). The ^1H n.m.r. spectrum of the bromomethoxy-compound (28) shows the signal from 2-H as a singlet, indicating that the five-membered ring *endo*-conformation is still preferred despite the absence of hydrogen bonding.

In a complementary way, the opening of the epoxide ring in the 6-*endo*-alkoxy-2,3-*endo*-epoxides (30) and (31) is highly regioselective because the transition state leading to the respective 3-*endo*-alcohols (19) and (20) (path A in the Figure; *endo*-envelope cyclopentane ring) is much preferred to the transition state leading to the 2-*endo*-alcohols (24) and (25) (path B in the Figure; *exo*-envelope cyclopentane ring). This rationale requires that only *trans*-diaxial opening of the epoxide takes place and that the transition state is product-like in character.[8]

The 6-*exo*-alkoxybicycloheptenes (12) and (13) are brominated non-specifically. We believe that this reflects a different conformation of the four-membered ring when a 6-*exo*-substituent is present. The larger coupling constants $J_{1,5}$ and smaller coupling constants $J_{1,7endo}$ suggest that the conformation of the four-membered ring is more nearly planar than in the 6-*endo*-substituted compounds. This conformational change in the four-membered ring and the consequent change in the torsion angle between C-1 and C-5 leads to exposure of the alkene unit to attack by bromine on the *endo*-face. The C-1–C-7 bond and 7-H no longer afford complete protection of the double bond on this face. The 2-*exo*-bromo-3-*endo*-hydroxy-compound (17) can exist in two extreme conformations and molecular models suggest that, for small torsion angles about the bridging C-1–C-5 bond, both conformations can be readily accommodated. ^1H N.m.r. spectroscopy suggested that the bromohydrin (17) prefers the conformation with the five-membered ring in the *exo*-envelope form ($J_{2,1}$ = $J_{2,3}$ = 4 Hz). Certainly, two transition states are involved in the opening of the epoxide ring in compounds (32) and (33) with the cuprate reagent, and the product distribution indicates that paths C and D (Figure) are equally favoured.

The bicycloheptene epoxide (29), unsubstituted at C-6, gave a product ratio (3-ol : 2-ol = 73 : 27) intermediate between the values for the 6-*endo*-alkoxy-compounds (3-ol : 2-ol = 97—85 : 3—15) and those for the 6-*exo*-alkoxy-compounds (3-ol : 2-ol = *ca.* 50 : 50). Similarly, ^1H n.m.r. spectroscopy indicated a *ca.* 50 : 50 population of *exo*- and *endo*-envelope conformations in the five-membered ring of the

bromohydrin (14), intermediate between the *endo*-envelope form as seen in compound (16) and the *exo*-envelope form as observed for the bromohydrin (17). Hence it is apparent that a 6-alkoxy-substituent in a bicyclo[3.2.0]heptane influences (i) the selectivity of electrophilic attack at a Δ^2-alkene unit; (ii) the preferred conformation of at least some 2-*exo*-, 3-*endo*-disubstituted derivatives, and (iii) the regioselectivity of nucleophilic attack on the 2,3-epoxide.

This interesting perannular conformational control did not aid our synthetic programme: reaction of the 2,3-*endo*-epoxy-6-*endo*-methoxy-bicycloheptane (30) with the cuprate reagent (2) gave two products in the ratio 84 : 16. The major product was identified as the 3-hydroxy-compound (38). The minor component was presumably the 2-hydroxy-isomer (39). This ratio was the same as that obtained on reaction of the acetal (1) with the cuprate reagent (2). Obviously the epoxy-acetal (1) prefers to react with the cuprate reagent through a conformation corresponding to that shown in path A in the Figure.

Experimental

^{1}H N.m.r. spectra were recorded for solutions in $CDCl_3$ unless otherwise stated, using $SiMe_4$ as internal reference, on Varian EM360 (60 MHz) and Bruker Spectrospin (250 and 400 MHz) spectrometers. I.r. spectra were recorded on a Perkin-Elmer 257 or a Unicam SP200 spectrophotometer, as liquid films (oils) or Nujol mulls (solids). The mass spectral and accurate mass determinations were achieved using AEI MS12 and MS902S spectrometers, respectively. M.p.s are uncorrected.

Thin-layer chromatography (t.l.c.) was carried out using Camlab 'Polygram' precoated silica-gel plates. Merck Kieselgel 60H was used for column chromatography.[9] Light petroleum refers to the fraction of b.p. 40—60 °C unless stated otherwise. All solvents for chromatography were distilled before use. All bicycloheptane derivatives described are enantiomeric mixtures.

Bicyclo[3.2.0]*hept-2-en-6-ols* (8) *and* (11).[4]—Bicyclo[3.2.0]-hept-2-en-6-one [10] (27 g, 250 mmol) was added during 2 h to a cooled, stirred suspension of sodium borohydride (9.5 g, 250 mmol) in ethanol (150 ml), after which excess of solvent was removed by distillation. The residue was treated with 2M hydrochloric acid (100 ml) and was extracted with diethyl ether (3 × 300 ml). The combined extracts were washed in turn with aqueous sodium hydrogen carbonate (100 ml) and water (3 × 300 ml) and were then dried ($MgSO_4$) and evaporated to dryness. The residue was distilled under reduced pressure to give a mixture of the *endo*- and *exo*-bicyclic alcohols (8) and (11), respectively (17.9 g, 65%), b.p. 63—65 °C at 6 mmHg. Short-path column chromatography of the mixture (5 g) over silica gel with 6% diethyl ether in light petroleum as eluant gave bicyclo[3.2.0]hept-2-en-6-*endo*-ol (8) (3.56 g, 71%) as an oil, $\nu_{max.}$ (cm^{-1}) 3 450 and 3 150; δ (60 MHz) 5.75 (2 H, s, 2- and 3-H), 4.40 (1 H, m, 6-H), and 3.33—1.30 (total 7 H, m, remaining protons).

Later fractions yielded bicyclo[3.2.0]hept-2-en-6-*exo*-ol (11) (0.58 g, 12%) as an oil, $\nu_{max.}$ (cm^{-1}) 3 450 and 3 150; δ (60 MHz) 5.66 (2 H, m, 2- and 3-H), 3.90 (1 H, td, *J* 8 and 4 Hz, 6-H), 3.66 (1 H, s, OH), 3.30—2.55 (2 H, m, 1- and 5-H), and 2.50—1.90 (total 4 H, m, remaining protons).

6-Methoxybicyclo[3.2.0]*hept-2-enes* (9) *and* (12).—A two-phase system, consisting of a solution of the alcohol to be methylated, tetrabutylammonium iodide (0.1 equiv.) in light petroleum (b.p. 30—40 °C), and 50% aqueous sodium hydroxide (2.6 equiv.), was equilibrated by being vigorously stirred for 30 min. Dimethyl sulphate (1.5 equiv.) was then added dropwise during 5 h. The mixture was stirred for a further 18 h and then ammonia solution (*d* 0.880) was added. After being stirred for 1 h the mixture was poured into water (50 ml). The organic phase was separated and washed with water (2 × 100 ml), and the aqueous washings were back-extracted with diethyl ether (2 × 50 ml). The combined organic fractions were dried ($MgSO_4$) and evaporated to dryness.

6-exo-*Methoxybicyclo*[3.2.0]*hept-2-ene* (12). The product from bicyclo[3.2.0]hept-2-en-6-*exo*-ol (11) (3.3 g, 30 mmol) gave, after Kugelrohr distillation (oven temperature 150—160 °C), the *title compound* (12) (62%) as an oil, $\nu_{max.}$ (cm^{-1}) 3 000 and 1 200; δ (60 MHz) 5.70 (2 H, m, 2- and 3-H), 3.85—3.30 (1 H, m, 6-H), 3.15 (3 H, s, OMe), and 3.10—1.90 (total 6 H, remaining protons) [Found: M^+, 124.0887. $C_8H_{12}O$ requires *M*, 124.0888].

6-endo-*Methoxybicyclo*[3.2.0]*hept-2-ene* (9). The product from bicyclo[3.2.0]hept-2-en-6-*endo*-ol (8) (1.76 g, 16 mmol) gave, after Kugelrohr distillation (oven temperature 140—150 °C), the *title compound* (9) (1.50 g, 76%) as an oil, $\nu_{max.}$ (cm^{-1}) 3 000 and 1 220; δ (60 MHz) 5.76 (2 H, s, 2- and 3-H), 3.97 (1 H, m, 6-H), 3.14 (3 H, s, OMe), and 3.10—1.40 (total 6 H, m, remaining protons) [Found: M^+, 124.0886. $C_8H_{12}O$ requires *M*, 124.0888].

6-Trityloxybicyclo[3.2.0]*hept-2-enes* (10) *and* (13).—A solution of the mixture of bicyclic alcohols (8) and (11) (7.5 g, 68 mmol), trityl chloride (21.0 g, 76 mmol), triethylamine (18 ml), and 4-(dimethylamino)pyridine (0.5 g, 2.5 mmol) in dichloromethane (150 ml) was refluxed under nitrogen. After 18 h the solution was poured into water and the mixture was extracted with chloroform. The extract was dried ($MgSO_4$) and evaporated to dryness. Short-path column chromatography of the residue over silica gel, with 5% ethyl acetate in light petroleum as eluant, gave a mixture of the ethers (10) and (13) (18.1 g, 75%). Rechromatography over silica gel with light petroleum as eluant then gave 6-endo-*trityloxybicyclo*[3.2.0]-*hept-2-ene* (10) (15.2 g), as crystals, m.p. 71—73 °C; $\nu_{max.}$ (cm^{-1}) 3 075, 2 950, 1 600, 1 500, and 1 460; δ (60 MHz), 7.60—7.10 (15 H, m, CPh_3), 5.80—5.60 (2 H, m, 2- and 3-H), 4.50—4.10 (1 H, m, 6-H), and 3.20—0.60 (total 6 H, m, remaining protons) [Found: M^+, 352.1820. $C_{26}H_{24}O$ requires *M*, 352.1826].

From later fractions 6-exo-*trityloxybicyclo*[3.2.0]*hept-2-ene* (13) (2.9 g) was isolated as crystals, m.p. 100 °C; $\nu_{max.}$ (cm^{-1}) 3 075, 2 950, 1 600, 1 500, and 1 460; δ (60 MHz), 7.7—7.1 (15 H, m, CPh_3), 5.70—5.35 (2 H, m, 2- and 3-H), 4.0—3.6 (1 H, m, 6-H), 3.2—2.6 (2 H, m, 1- and 5-H), and 2.6—0.7 (total 4 H, m, remaining protons) [Found: M^+, 352.1824. $C_{26}H_{24}O$ requires *M*, 352.1826].

General Procedure for the Preparation of the Bromohydrins (14) *and* (15).—The appropriate bicycloheptene was dissolved in a mixture of acetone (40 ml) and water (10 ml). NBA (1.25 equiv.) was then added to the stirred solution. After 18 h at room temperature the mixture was treated with water (10 ml) and the acetone was removed under reduced pressure. Diethyl ether (40 ml) was added to the aqueous residue and the organic phase was separated and washed with water (3 × 30 ml). The aqueous washings were back-extracted with diethyl ether (2 × 30 ml). The combined organic fractions were dried ($MgSO_4$) and evaporated to dryness.

2-exo-*Bromobicyclo*[3.2.0]*heptan*-3-endo-*ol* (14). The product from bicyclo[3.2.0]hept-2-ene [3] (7) (2.5 g, 27 mmol) gave, after Kugelrohr distillation (oven temperature 95—100 °C at 10^{-2} mmHg), a mixture of bromohydrins (3.5 g, 69%). The mixture was partially separated by column chromatography over silica gel with 2% ethyl acetate in light petroleum as eluant

to give 2-exo-*bromobicyclo*[3.2.0]*heptan*-3-endo-*ol* (14) (1.05 g) as an oil, $\nu_{max.}$ (cm^{-1}) 3 400br, 2 975, 1 290, and 1 180; δ (250 MHz) 4.58 (1 H, dt, *J* 5, 2.5, and 2.5 Hz, 3-H), 4.18 (1 H, t, *J* 2.5 and 2.5 Hz, 2-H), 3.2—2.9 (2 H, m, 1- and 5-H), 2.42 (1 H, ddd, *J* 14, 8.5, and 5 Hz, 4-H_{exo}), and 2.3—1.7 (total 5 H, m, remaining protons) (Found: C, 43.8; H, 5.8. $C_7H_{11}BrO$ requires C, 44.0; H, 5.8%).

Later fractions gave compound (14) together with other, isomeric bromohydrins (2.11 g), $\nu_{max.}$ (cm^{-1}) (3 400br, 2 975, 1 290, and 1 180 ; ^1H n.m.r. spectrum showed two major components (Found: C, 44.4; H, 6.1. Calc. for $C_7H_{11}BrO$: C, 44.0; H, 5.8%).

2-exo-*Bromo*-6-endo-*methoxybicyclo*[3.2.0]*heptan*-3-endo-*ol* (15). The product from 6-*endo*-methoxybicyclo[3.2.0]hept-2-ene (1.5 g, 12 mmol) gave, after column chromatography with 6% diethyl ether in light petroleum ether as eluant, 2-exo-*bromo*-6-endo-*methoxybicyclo*[3.2.0]*heptan*-3-endo-*ol* (15) (2.18 g, 82%) as a straw-coloured oil, $\nu_{max.}$ (cm^{-1}) 3 400br and 1 200; δ (60 mHz) 4.70—3.60 (total 4 H, m, 2-, 3-, and 6-H and OH), 3.36 (3 H, s, OMe), and 3.32—1.70 (total 6 H, m, remaining protons) (Found: C, 43.4; H, 6.0. $C_8H_{13}BrO_2$ requires C, 43.5; H, 5.9%).

General Procedure for Preparation of the Bromohydrins (16) *and* (17).—The corresponding bicycloheptene was dissolved in a mixture of acetone (40 ml) and water (5 ml). NBS (1.5 equiv.) was added to the stirred solution. After 48 h at room temperature in the dark, aqueous sodium hydrogen carbonate (8%; 10 ml) was added and the acetone was removed under reduced pressure. Diethyl ether (40 ml) was added to the aqueous residue and the organic phase was separated and washed with water (2 × 50 ml). The aqueous washings were back-extracted with diethyl ether (2 × 30 ml). The combined organic fractions were dried ($MgSO_4$) and evaporated to dryness.

2-exo-*Bromo*-6-endo-*trityloxybicyclo*[3.2.0]*heptan*-3-endo-*ol* (16). The product from 6-*endo*-trityloxybicyclo[3.2.0]hept-2-ene (10) (1.8 g, 5 mmol) gave 2-exo-*bromo*-6-endo-*trityloxybicyclo*[3.2.0]*heptan*-3-endo-*ol* (16) as crystals (1.52 g, 67%), m.p. 153 °C (aqueous acetone); $\nu_{max.}$ (cm^{-1}) 3 425, 3 025, 2 950, 1 490, and 1 450; δ (250 MHz) 7.5—7.2 (15 H, m, CPh_3), 4.49 (1 H, ddq, $J_{3,4exo}$ 5, $J_{3,4endo}$ 1, and $J_{2,3}$ <1 Hz, 3-H), 4.31 (1 H, td, $J_{5,6}$ 8.5, $J_{6,7endo}$ 8.5, and $J_{6,7endo}$ 5.5 Hz, 6-H), 4.2 (1 H, d, OH), 4.14 (1 H, s, 2-H), 3.08 (1 H, tdq, $J_{4exo,5}$ 8.5, $J_{1,5}$ 6.5, and $J_{4endo,5}$ 1.5 Hz, 5-H), 2.65 (1 H, td, $J_{1,7exo}$ 9.5, $J_{1,7endo}$ 6.5, and $J_{1,2}$ <1 Hz, 1-H), 2.36 (1 H, ddd, $J_{4endo,4exo}$ 15 Hz, 4-H_{exo}), 2.22 (1 H, dq, 4-H_{endo}), 2.02 (1 H, dddd, $J_{7exo,7endo}$ 14 Hz, 7-H_{exo}), and 1.80 (1 H, dtd, 7-H_{endo}) (Found: C, 69.5; H, 5.6. $C_{26}H_{25}BrO_2$ requires C, 69.5; H, 5.6%).

2-exo-*Bromo*-6-exo-*trityloxybicyclo*[3.2.0]*heptan*-3-endo-*ol* (17). The product from 6-*exo*-trityloxybicyclo[3.2.0]hept-2-ene (13) (1.0 g, 3 mmol) gave a gum containing a mixture of bromohydrins (0.97 g, 76%). These were partially separated by short-path chromatography over silica gel with 1% ethyl acetate in light petroleum as eluant to give the less polar, major isomer, 2-exo-*bromo*-6-exo-*trityloxybicyclo*[3.2.0]*heptan*-3-endo-*ol* (17) (0.60 g, 62%) as a solid, m.p. 127—128 °C (aqueous acetone); $\nu_{max.}$ (cm^{-1}) 3 400br, 2 950, 1 490, and 1 450; δ (250 MHz) 7.8—7.5 (15 H, m, CPh_3), 4.22 (1 H, dt, $J_{3,4exo}$ 6.5, $J_{3,4endo}$ 5, and $J_{2,3}$ 4 Hz, 3-H), 4.04 (1 H, ddd, $J_{6,7endo}$ 7.5, $J_{6,7exo}$ 5.5, and $J_{5,6}$ 4 Hz, 6-H), 3.82 (1 H, t, $J_{1,2}$ 4 Hz, 2-H), 2.88 (1 H, tt, $J_{1,7exo}$ 10, $J_{1,5}$ 9, and $J_{1,7endo}$ 4.5 Hz, 1-H), 2.65 (1 H, m, 5-H), 2.12 (1 H, dddd, $J_{7,endo,7exo}$ 13.5 and $J_{5,7exo}$ 1 Hz, 7-H_{exo}), 2.0 (1 H, dddd, $J_{5,7endo}$ 1 Hz, 7-H_{endo}), 1.87 (1 H, ddd, $J_{4exo,4endo}$ 14.5 and $J_{4exo,5}$ 9 Hz, 4-H_{exo}), and 0.94 (1 H, ddd, $J_{4endo,5}$ 3 Hz, 4-H_{endo}) (Found: C, 69.4; H, 5.7. $C_{26}H_{25}BrO_2$ requires C, 69.5; H, 5.6%). Further elution gave a mixture of compound (17) with the isomeric bromohydrin(s) (0.37 g, 38%).

2-exo-*Bromo*-3-endo-*methoxy*-6-endo-*trityloxybicyclo*[3.2.0]*heptane* (28).—To a stirred 6-*endo*-trityloxybicyclo[3.2.0]hept-2-ene (10) (1.2 g, 3.4 mmol) in methanol (100 ml) was added NBS (0.8 g, 4.5 mmol). After 3 h at room temperature the mixture was treated with sodium hydrogen carbonate (0.38 g, 4.5 mmol) and the methanol removed under reduced pressure. Water (100 ml) was added to the residue and the mixture was extracted with diethyl ether (3 × 100 ml). The combined organic extracts were dried ($MgSO_4$) and evaporated to dryness. The solid residue was recrystallized from methanol–dichloromethane to give 2-exo-*bromo*-3-endo-*methoxy*-6-endo-*trityloxybicyclo*[3.2.0]*heptane* (28) (1.05 g, 69%) as crystals, m.p. 90—92 °C; $\nu_{max.}$ (cm^{-1}) (0.5% $CHBr_3$ solution) 2 820, 1 075, 755, and 700; δ (250 MHz), 7.6—7.2 (15 H, m, CPh_3), 4.1 (1 H, s, 2-H), 4.05—4.00 (2 H, m, 3- and 6-H), 3.40 (3 H, s, OMe), 2.45—2.00 (total 5 H, m, 1-, 5-, 4_{endo}, 7_{exo}, and 7-H_{endo}), and 1.8 (1 H, ddd, *J* 15, 10, and 6.5 Hz, 4-H_{exo}) (Found: C, 69.75; H, 5.85. $C_{27}H_{27}BrO_2$ requires C, 70.0 H, 5.85%).

General Procedure for the Preparation of the 2,3-*Epoxybicyclo*[3.2.0]*heptanes* (29)—(31), (33), (34), *and* (36).—The appropriate bromohydrin was stirred at 0 °C in dry diethyl ether (50 ml) and potassium t-butoxide (1.5 equiv.) was added in one portion. The mixture was stirred for a further 3—18 h at room temperature. Water (100 ml) was then added and the mixture was extracted with diethyl ether (3 × 50 ml). The combined ethereal extracts were dried ($MgSO_4$) and the diethyl ether was removed by distillation to give the corresponding epoxide.

2,3-*Epoxybicyclo*[3.2.0]*heptanes* (29) *and* (34). The mixture of bromohydrins obtained from the alkene (7) (9 g, 47 mmol) gave, after Kugelrohr distillation (oven temperature 120—130 °C at 50 mmHg), a mixture of the bicyclic epoxides (29) and (34) (2.0 g, 39%) in the ratio 95 : 5 (by 250-MHz ^1H n.m.r. spectroscopy). Column chromatography of the mixture over silica gel with 2% ethyl acetate in light petroleum as eluant gave 2,3-endo-*epoxybicyclo*[3.2.0]*heptane* (29) (0.95 g) as an oil, δ ($CDCl_3$) 3.7br (1 H, s, 3-H), 3.56 (1 H, t, 2-H), 2.87 (1 H, quintet, 5-H), 2.70 (1 H, t, 1-H), and 2.3—1.6 (total 6 H, m, remaining protons) (Found: M^+, 110.0731. $C_7H_{10}O$ requires *M*, 110.0731).

2,3-exo-*Epoxybicyclo*[3.2.0]*heptane* (34) (10 mg) was obtained from later fractions as an oil, δ ($CDCl_3$) 3.60 (1 H, t, 3-H), 3.40 (1 H, d, 2-H), 2.92 (1 H, q, 5-H), 2.59 (1 H, m, 1-H), and 2.3—1.6 (total 6 H, m, remaining protons) {Found (c.i.m.s. NH_3): $[M + NH_4]^+$, 128.1075, $[M + H]^+$, 111.0809. C_7H_{10} requires $[M + NH_4]$, *m/z* 128.1076, $[M + H]$, *m/z* 111.0870}.

2.3-endo-*Epoxy*-6-endo-*methoxybicyclo*[3.2.0]*heptane* (30). The product from 2-*exo*-bromo-6-*endo*-methoxybicyclo[3.2.0]heptan-3-*endo*-ol (15) (3.2 g, 15 mmol) gave, after Kugelrohr distillation (oven temperature 80—85 °C at 14 mmHg), 2,3-endo-*epoxy*-6-endo-*methoxybicyclo*[3.2.0]*heptane* (30) (1.59 g, 80%) as an oil, δ (60 MHz) 4.00—3.13 (total 4 H, m, 1-, 2-, 3-, and 6-H), 3.06 (3 H, s, OMe), and 2.76—1.36 (total 5 H, remaining protons) (Found: C, 68.4; H, 8.95. $C_8H_{12}O_2$ requires C, 68.55; H, 8.6%).

2,3-endo-*Epoxy*-6-endo-*trityloxybicyclo*[3.2.0]*heptane* (31). The product from 2-*exo*-bromo-6-*endo*-trityloxybicyclo[3.2.0]-heptan-3-*endo*-ol (2.1 g, 5 mmol) gave the *title compound* (1.4 g, 80%) as crystals, m.p. 115 °C (hexane–chloroform); δ (60 MHz) 7.60—7.00 (15 H, m, CPh_3), 4.8—4.3 (1 H, m, 6-H), 3.6—3.2 (2 H, m, 2- and 3-H), and 3.00—1.40 (total 6 H, m, remaining protons) (Found: C, 84.75; H, 6.5. $C_{26}H_{24}O_2$ requires C, 84.75; H, 6.55%).

2,3-endo-*Epoxy*-6-exo-*trityloxybicyclo*[3.2.0]*heptane* (33). The product from 2-*exo*-bromo-6-*exo*-trityloxybicyclo[3.2.0]-

heptan-3-*endo*-ol (17) (0.5 g, 1.1 mmol) gave 2,3-endo-*epoxy*-6-exo-*trityloxybicyclo*[3.2.0]*heptane* (33) (0.31 g, 75%) as crystals, m.p. 123—126 °C (hexane–ethyl acetate); δ (250 MHz) 7.50—7.10 (15 H, m, CPh_3), 3.81 (1 H, q, 6-H), 3.40 (1 H, m, 3-H), 3.29 (1 H, t, 2-H), 2.70 (1 H, td, 5-H), 2.48 (1 H, tt, 1-H), 1.95—1.86 (2 H, m, 7-H_2), 1.38 (1 H, ddd, 4-H_{exo}), and 1.05 (1 H, d, 4-H_{endo}) (Found: C, 84.2; H, 6.7. $C_{26}H_{24}O_2$ requires C, 84.75; H, 6.55%).

2,3-exo-*Epoxy*-6-exo-*trityloxybicyclo*[3.2.0]*heptane* (36). The mixed fractions obtained from the chromatographic purification of the bromohydrin (17) (see above) (0.37 g, 0.82 mmol) gave a two-component mixture of isomeric epoxides (0.244 g, 80%) which, after column chromatography over silica gel with ethyl acetate–light petroleum as eluant, furnished crystals of compound (33) (0.071 g, 30%), m.p. 125 °C.

Later fractions contained 2,3-exo-*epoxy*-6-exo-*trityloxybicyclo*[3.2.0]*heptane* (36) (0.171 g, 70%) which was isolated as a gum, δ (60 MHz) 7.55—7.20 (15 H, m, CPh_3), 3.95—3.70 (1 H, m, 6-H), 3.45—3.15 (2 H, m, 2- and 3-H), and 2.90—0.95 (total 6 H, m, remaining protons) (Found: C, 83.95; H, 7.3. $C_{26}H_{24}O_2$ requires C, 84.75; H, 6.55%).

2,3-*Epoxy*-6-exo-*methoxybicyclo*[3.2.0]*heptanes* (32) *and* (35).—To a stirred solution of 6-*exo*-methoxybicyclo[3.2.0]-hept-2-ene (12) (2.2 g, 18 mmol) in a mixture of acetone (60 ml) and water (15 ml) was added NBA (3.06 g, 22 mmol). The mixture was kept for 18 h at room temperature, water (10 ml) was added, and the acetone was removed under reduced pressure. Diethyl ether (40 ml) was added and the organic phase was separated and washed with water (3 × 40 ml). The aqueous washings were back-extracted with diethyl ether (2 × 30 ml). The combined organic extracts were dried ($MgSO_4$) and evaporated to dryness to give, after chromatography over silica gel with ethyl acetate–light petroleum as eluant, a mixture of 6-*exo*-methoxybicyclic bromohydrins (3.5 g, 89%).

This mixture was stirred at 0 °C in dry diethyl ether (50 ml), potassium t-butoxide (2.71 g, 1.5 equiv.) was added in one portion, and the mixture was stirred for 6 h at room temperature. Water (100 ml) was then added and the mixture was extracted with diethyl ether (3 × 100 ml). The combined ethereal extracts were dried ($MgSO_4$) and evaporated to dryness to give an oil containing two isomeric epoxides (1.12 g, 54%). Chromatography with 5% ethyl acetate in light petroleum as eluant gave 2,3-endo-*epoxy*-6-exo-*methoxybicyclo*[3.2.0]-*heptane* (32) (435 mg, 85%) as an oil, δ (60 MHz) 3.73—3.35 (total 4 H, m, 1-, 2-, 3-, and 6-H), 3.18 (3 H, s, OMe), and 2.80—1.00 (total 5 H, m, remaining protons) (Found: C, 68.4; H, 8.9. $C_8H_{12}O_2$ requires C, 68.55; H, 8.6%).

Later fractions gave 2,3-exo-*epoxy*-6-exo-*methoxybicyclo*-[3.2.0]*heptane* (35) (72.5 mg, 15%) as an oil, δ (60 MHz) 3.78—3.37 (total 4 H, m, 1-, 2-, 3-, and 6-H), 3.23 (3 H, s, OMe), and 3.10—1.10 (total 5 H, m, remaining protons) (Found: C, 68.25; H, 8.5. $C_8H_{12}O_2$ requires C, 68.55; H, 8.6%).

Lithium Dibutyl Cuprate Reagent.—Copper(I) bromide–dimethyl sulphide complex (CuBr–Me_2S) [11] (1 equiv.), dissolved in dimethyl sulphide, was slowly added to an ethereal solution of n-butyl-lithium–hexane (1.5M; 2 equiv.) at −78 °C under nitrogen. After being stirred for 30 min at −78 °C the ethereal solution of lithium dibutyl cuprate was ready for immediate use.

General Procedure for the Preparation of the Bicyclic Alcohols (18)—(27).—A solution of the appropriate epoxide in anhydrous diethyl ether was slowly added during 10 min to a stirred solution of lithium dibutyl cuprate reagent (1.25 equiv.) at −78 °C under nitrogen. The solution was maintained at −78 °C for a further 3 h and was then warmed to −10 °C during 18 h. Saturated aqueous ammonium chloride was then added and the whole mixture was stirred for a further 2 h at room temperature. The organic layer was separated, washed in turn with 2M sulphuric acid, aqueous sodium hydrogen carbonate, and water, and was then dried ($MgSO_4$) and evaporated to dryness. The following alcohols were thus prepared.

2-exo-*Butylbicyclo*[3.2.0]*heptan*-3-endo-*ol* (18) *and* 3-exo-*butylbicyclo*[3.2.0]*heptan*-2-endo-*ol* (23). The product from 2,3-*endo*-epoxybicyclo[3.2.0]heptane (29) (0.50 g, 4.5 mmol) gave, after chromatography over silica gel with ethyl acetate–light petroleum as eluant, a mixture of isomers (18) and (23) (0.49 g; homogeneous by t.l.c.) in the ratio 73 : 27 (g.l.c. using an SP 2100 capillary column programmed at 2 °C min^{-1} from 80 to 150 °C).

Huang-Minlon-modified Wolff-Kishner reduction of the ketone (37) [5] (see below) gave a product identical (g.l.c.) with the major component, 2-exo-*butylbicyclo*[3.2.0]*heptan*-3-endo-*ol* (18), $\nu_{max.}$ (cm^{-1}) 3 400br, 2 950, 2 875, 1 470, and 1 080; δ (60 MHz) 3.90 (1 H, q, 3-H) and 2.90—0.70 (total 19 H, m, remaining protons) [G.l.c.–m.s. gave, for compound (18), M^+, 168.1536 and, for its isomer (23), M^+, 168.1524. $C_{11}H_{20}O$ requires *M*, 168.1515].

2-exo-*Butyl*-6-endo-*methoxybicyclo*[3.2.0]*heptan*-3-endo-*ol* (19) *and* 3-exo-*butyl*-6-endo-*methoxybicyclo*[3.2.0]*heptan*-2-endo-*ol* (24). The product from 2,3-*endo*-epoxy-6-*endo*-methoxybicyclo[3.2.0]heptane (30) (500 mg, 3.6 mmol) gave, after column chromatography over silica gel with 6% diethyl ether in light petroleum as eluant, a mixture of the isomers (19) and (24) (72%; homogeneous by t.l.c.) in the ratio 97 : 3 (g.l.c., CP Wax 51, 80 °C for 1 min then at 5 °C min^{-1} to 180 °C). Spectroscopic data (400-MHz ^1H n.m.r. spectroscopy) showed the major isomer to be 2-*exo*-butyl-6-*endo*-methoxybicyclo[3.2.0]heptan-3-*endo*-ol (19), $\nu_{max.}$ (cm^{-1}) 3 400br, 2 925, 2 875, and 1 120; δ 3.99br (1 H, s, 3-H), 3.90 (1 H, tdd, *J* 8, 8, 5, and 1 Hz, 6-H), 3.71br (1 H, s, OH), 3.25 (3 H, s, OMe), 3.18 (s, OMe of isomer), 3.06 (1 H, m, 5-H), 2.55 (1 H, dtd, *J* 13. 8.5, 8.5, and 2 Hz, 7-H_{exo}), 2.22 (1 H, q, *J* 7, 7, and 7 Hz, 1-H), 2.00—1.92 (total 3 H, m, 7-H_{endo} and 4-H_2), 1.82 (1 H, t, *J* 7.5 and 7.5 Hz, 2-H), and 1.28—0.70 (total 9 H, m, $CH_2CH_2CH_2Me$) [G.l.c.–m.s. studies on the major component gave M^+, 198.1585. Calc. for $C_{12}H_{22}O_2$: *M*, 198.1620.]

2-exo-*Butyl*-6-endo-*trityloxybicyclo*[3.2.0]*heptan*-3-endo-*ol* (20) *and* 3-exo-*butyl*-6-endo-*trityloxybicyclo*[3.2.0]*heptan*-2-endo-*ol* (25). The product from 2,3-*endo*-epoxy-6-*endo*-trityloxybicyclo[3.2.0]heptane (31) (600 mg, 1.6 mmol) gave a mixture, g.l.c. analysis of which (C.P. Si15; 250 °C for 2 min, then to 325 °C at 5 °C min^{-1}; trimethylsilyl ether derivative) showed the presence of two polar components in the ratio 85 : 15. The mixture was separated by chromatography over silica gel with light petroleum as eluant to give the starting epoxide (31) (84 mg recovery), followed by 2-exo-*butyl*-6-endo-*trityloxybicyclo*[3.2.0]*heptan*-3-endo-*ol* (20) (388 mg, (64%) as a gum, $\nu_{max.}$ (cm^{-1}) 3 400br, 3 075, 2 950, and 2 850; δ (250 MHz), 7.50—7.15 (15 H, m, CPh_3), 4.19 (1 H, m, 6-H), 3.92br [1 H, s (dt after D_2O shake *J* 6, 3, and 3 Hz), 3-H], 3.18br (1 H, d, OH), 2.60 (1 H, m, 5-H), 2.12—2.07 (total 2 H, m, 1- and 4-H_{endo}), 1.90—1.65 (total 4 H, m, 2-H, 4-H_{exo}, and 7-Hz), 1.30—1.00 (total 6 H, m, $[CH_2]_3$), and 0.85 (3 H, m, CH_2Me) (Found: C, 84.2; H, 8.0. $C_{30}H_{34}O_2$ requires C, 84.45; H, 8.05%).

3-exo-*Butyl*-6-endo-*trityloxybicyclo*[3.2.0]*heptan*-2-endo-*ol* (25) (66 mg, 12%) was eluted last and was obtained as a gum, $\nu_{max.}$ (cm^{-1}) 3 400br, 3 075, 2 950, and 2 850; δ (250 MHz) 7.50—7.15 (15 H, m, CPh_3), 4.20 (1 H, q, 6-H), 3.58 (1 H, dd, *J* 9 and 7 Hz, 2-H), 2.38 (1 H, m, 5-H), and 2.30—0.80

(total 16 H, m, remaining protons) (Found: C, 84.25; H, 8.0. $C_{30}H_{34}O_2$ requires C, 84.45; H, 8.05%).

2-exo-*Butyl*-6-exo-*methoxybicyclo*[3.2.0]*heptan*-3-endo-*ol* (21) *and* 3-exo-*butyl*-6-exo-*methoxybicyclo*[3.2.0]*heptan*-2-endo-*ol* (26). The product from 2,3-*endo*-epoxy-6-*exo*-methoxybicyclo[3.2.0]heptane (32) (350 mg, 2.7 mmol), gave, after column chromatography over silica gel with 6% diethyl ether in light petroleum as eluant, the isomers (21) and (26) (72%; homogeneous by t.l.c.) in the ratio 55 : 45 (g.l.c., 12 M SP2100 capillary; 40 ⟶ 90 °C at 12 °C min^{-1}, then at 1.5 °C min^{-1} to 100 °C, and finally at 5 °C min^{-1} to 140 °C); $\nu_{max.}$ (cm^{-1}) 3 400, 2 925, 2 850, and 1 100; δ (400 MHz) 3.93 [1 H, q, 3-H of (21)], 3.85 [1 H, dt, 6-H of (21)], 3.69 [1 H, dd, *J* 9 and 7.5 Hz, 2-H of (26)], 3.49 [1 H, ddd, *J* 7, 4.5 and 3 Hz, 6-H of (26)], 3.23 and 3.22 (together 6 H, 2 × s, OMe of (21) and (26)], and 3.0—0.8 (total 34 H, complex, remaining protons) (Found: C, 72.45; H, 11.2 Calc. for $C_{12}H_{22}O_2$: C, 72.7; H, 11.2%).

2-exo-*Butyl*-6-exo-*trityloxybicyclo*[3.2.0]*heptan*-3-endo-*ol* (22) *and* 3-exo-*butyl*-6-exo-*trityloxybicyclo*[3.2.0]*heptan*-2-endo-*ol* (27). The product from 2,3-*endo*-epoxy-6-*exo*-trityloxybicyclo[3.2.0]heptane (33) (83 mg, 0.23 mmol) gave, after chromatography over silica gel with ethyl acetate–light petroleum as eluant, the isomers (22) and (27) (87%; homogeneous by t.l.c.) in the ratio 55 : 45 (g.l.c., CPSil 5; trimethylsilyl ether derivative; 250 °C for 2 min, then at 5 °C min^{-1} to 325 °C); $\nu_{max.}$ (cm^{-1}) 3 400br, 2 950, and 2 825; δ (250 MHz) ([$^2H_6$]benzene) 7.66—6.95 (30 H, m, 2 × CPh_3), 4.23 [1 H, dt, 6-H of (22)], 3.88 [1 H, ddd, 6-H of (27)], 3.40 [1 H, q, $J_{2,3}$, $J_{3,4exo}$, and $J_{3,4endo}$ 6 5 Hz, 3-H of (22)], 3.29 [1 H, t, $J_{1,2}$ and $J_{2,3}$ 8 Hz, 2-H of (27)], and 2.65—0.70 (total 34 H, complex, remaining protons) (Found: C, 8.42; H, 8.25 Calc. for $C_{30}H_{34}O_2$: C, 8.45; H, 8.05%).

2-exo-[(3-*t*-*Butyldimethylsilyloxy*)*oct*-1-*enyl*]-6-endo-*methoxybicyclo*[3.2.0]*heptan*-3-endo-*ol* (38) *and* 3-exo-[(3-*t*-*Butyldimethylsilyloxy*)*oct*-1-*enyl*]-6-endo-*methoxybicyclo*-[3.2.0]*heptan*-2-endo-*ol* (39).—A solution of 2,3-*endo*-epoxy-6-*endo*-methoxybicyclo[3.2.0]heptane (30) (0.5 g, 3.9 mmol) in dry diethyl ether was added dropwise to a stirred solution of lithium 3-(t-butyldimethylsilyloxy)oct-1-enyl(pent-1-ynyl)-cuprate (2) [1] (1.25 equiv.) in dry diethyl ether at −78 °C under nitrogen. After 1 h the solution was warmed to −30 °C for 16 h. The reaction was quenched by the addition of saturated aqueous ammonium chloride and the whole mixture was stirred vigorously at room temperature. After 4 h the organic layer was separated and was washed with 2M sulphuric acid and the aqueous layer was back-extracted with diethyl ether. The combined ethereal fractions were washed in turn with 8% aqueous sodium hydrogen carbonate and water and were then dried ($MgSO_4$), and evaporated to dryness to give a pale-yellow oil. This contained a mixture of the isomers (38) and (39) in the ratio 84 : 16 (g.l.c., trimethylsilyl ether derivative; SP2100 capillary; 180 ⟶ 230 °C at 2 °C min^{-1}). Short-path column chromatography over silica gel with 20% ethyl acetate in light petroleum as eluant afforded a mixture of the isomers (38) and (39) (875 mg, 64%). These were partially separated by short-path chromatography on silica gel with 5% ethyl acetate in light petroleum as eluant to give the major isomer, 2-exo-[(3-*t*-*butyldimethylsilyloxy*)*oct*-1-*enyl*]-6-endo-*methoxybicyclo*[3.2.0]*heptan*-3-endo-*ol* (38), $\nu_{max.}$ (cm^{-1}) 3 450br, 2 975, 2 925, 2 850, 1 070, 840, and 780; δ (250 MHz) 5.3 (2 H, m, CH=CH), 4 05 (1 H, m, 3-H), 3 95—3.90 (total 2 H, m, 3'- and 6-H), 3.26 (3 H, s, OMe), 3.13 (1 H, m, 5-H), 2.65—2 50 (total 2 H, m, 2- and 7-H), 2.38 (1 H, m, 1-H), 2.05—1.90 (total 3 H, m, 4-H_2 and 7-H), 1.90—1.10 (total 8 H, m, $[CH_2]_4$), 0.85 (total 12 H, m, Bu^t and CH_2Me), and 0.20—0.01 (6 H, m, $SiMe_2$). The assignments were confirmed by decoupling techniques (Found: C, 69.1; H, 11.2. $C_{22}H_{42}O_3Si$ requires C, 69.05; H, 11.05%).

A mixture of compounds (38) and (39), rich in the latter component, was obtained from later fractions; $\nu_{max.}$ (cm^{-1}) 3 450br, 2 975, 2 925, 2 850, 1 070, 840, and 780; δ (60 MHz) 5.35—5.20 (2 H, m, CH=CH), 4.05—3.60 (3 H, complex), 3.2 (3 H, s, OMe), 3.2—1.9 (6 H, complex), 1.90—1.2 (total 8 H, m, $[CH_2]_4$), 0.9 (total 12 H, m, Bu^t and CH_2Me), and 0.20—0.10 (6 H, m, $SiMe_2$) (Found: C, 69.2; H, 11.25. $C_{22}H_{42}O_3Si$ requires C, 69.05; H, 11.05%).

2-exo-*Butylbicyclo*[3.2.0]*heptan*-3-endo-*ol* (18) *by Reduction of* 2-exo-*Butyl*-3-endo-*hydroxybicyclo*[3.2.0]*heptan*-6-*one* (37). —A mixture of the ketone (37) [5] (1.3 g, 7 mmol), potassium hydroxide (0.76 g, 14 mmol), triethylene glycol (20 ml), and hydrazine hydrate (85%; 1 ml) was refluxed for 1 h and was then distilled until the temperature of the distillate rose to 175—178 °C. The mixture was refluxed again for a further 3 h and was again distilled to 175—178 °C. The combined distillates were extracted with diethyl ether (3 × 100 ml) and the combined extracts dried ($MgSO_4$) and evaporated to dryness. Short-path chromatography with ethyl acetate–light petroleum as eluant gave 2-exo-*butylbicyclo*[3.2.0]*heptan*-3-endo-*ol* (18) as an oil (0.63 g, 53%), $\nu_{max.}$ (cm^{-1}) 3 400br, 2 950, 2 875, 1 470, and 1 080; δ (60 MHz) 3.90 (1 H, q, 3-H), 2.6br (1 H, s, OH), and 2.90—0.70 (total 18 H, complex, remaining protons) (Found: M^+, 168.1512 $C_{11}H_{20}O$ requires *M*, 168.1513). G.l.c. analysis (SP2100 capillary programmed at 2 °C min^{-1} from 80 to 150 °C) showed an identical retention time (6.7 min) for compound (18) and the major product obtained from the reaction of the epoxide (29) with the lithium dibutylcuprate reagent.

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