Formation of Bromohydrins and Epoxides from 4-Hydroxy-2-oxabicyclo[3.3.0]oct-7-en-3-one and 9-Hydroxy-7-oxabicyclo-[4.3.0]non-4-en-8-one

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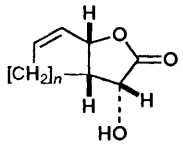
The hydroxy lactone **1** and the silylated derivative **8** react selectively with HOBr to give access to polyfunctional bicyclic systems such as the bromo ester **10**. The lactone **3** or the corresponding derivative **20** react less selectively to give mixtures of compounds **16**, **17**, **18**, **19**, **21**, **22**. The hydroxybicyclo[4.3.0]nonenones **2** and **4** behave in a similar fashion to the lactone **3**, reacting non-selectively with HOBr and *m*-chloroperbenzoic acid to produce a plethora of highly substituted bicyclo compounds **23**–**31**, **33**–**39**, **41** and **42**. X-Ray crystal structures were obtained for four compounds, the diacetates **25** and **37** and the epoxides **26** and **27**.

The hydroxy lactone **1** is easy to prepare,[1] can be resolved by enzyme-catalysed kinetic resolutions,[2] and has been used in these laboratories[3] and elsewhere[4] for the preparation of natural products and selected analogues in homochiral or racemic form. The isomeric compound **3** is also available although it is less easy to prepare (from cyclopentadiene and glyoxylic acid) in substantial quantities. The homologous hydroxy lactones **2** and **4** can be synthesized from cyclohexa-1,3-diene and glyoxylic acid in the prescribed fashion,[1] and the pure enantiomers of compound **2** have been obtained.[5]



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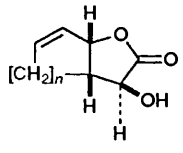
2 $n=2$



3 $n=1$
4 $n=2$

The carbocyclic ring of the lactones **1**–**4** contains an alkene unit which, ostensibly, has an exposed face and a (more or less) hindered face and it was of interest to us to investigate the selectivity of the attack on the unsaturated lactones **1**–**4** by electrophilic reagents.

Results

Treatment of the hydroxy lactone **1** with *N*-bromoacetamide (NBA) in aq. acetone furnished only the bromohydrin **5** (containing five contiguous chiral centres as shown in Scheme 1). The stereochemical relationships were clearly indicated by NMR data (see Experimental section).[6] Treatment of the bromohydrin **5** with base afforded the epoxide **6** while hydrodebromination using tributyltin hydride and azoisobutyronitrile (AIBN, cat.) provided the diol **7**. Similarly, the *tert*-butyldimethylsilyl ether **8**, derived from compound **1** in 90% yield, gave only the bromohydrin **9** on treatment with NBA in aq. acetone. The bromohydrin **9** was fully characterised as the ester **10**.

Hydrodebromination of the bromohydrin **9** gave the alcohol **11** which, in turn, was converted into the diastereoisomeric esters **12** and **13** as described in Scheme 1. Selective hydrolysis of the acetate unit in compound **13** proved difficult, so access to the corresponding alcohol **14** was better effected *via* the corresponding, more easily hydrolysed, chloroacetate. The ester **12** was also obtained, albeit in modest yield, on treatment of the silylated compound **8** with mercury(II) acetate, followed by sodium borohydride reduction and a standard acetylation procedure.

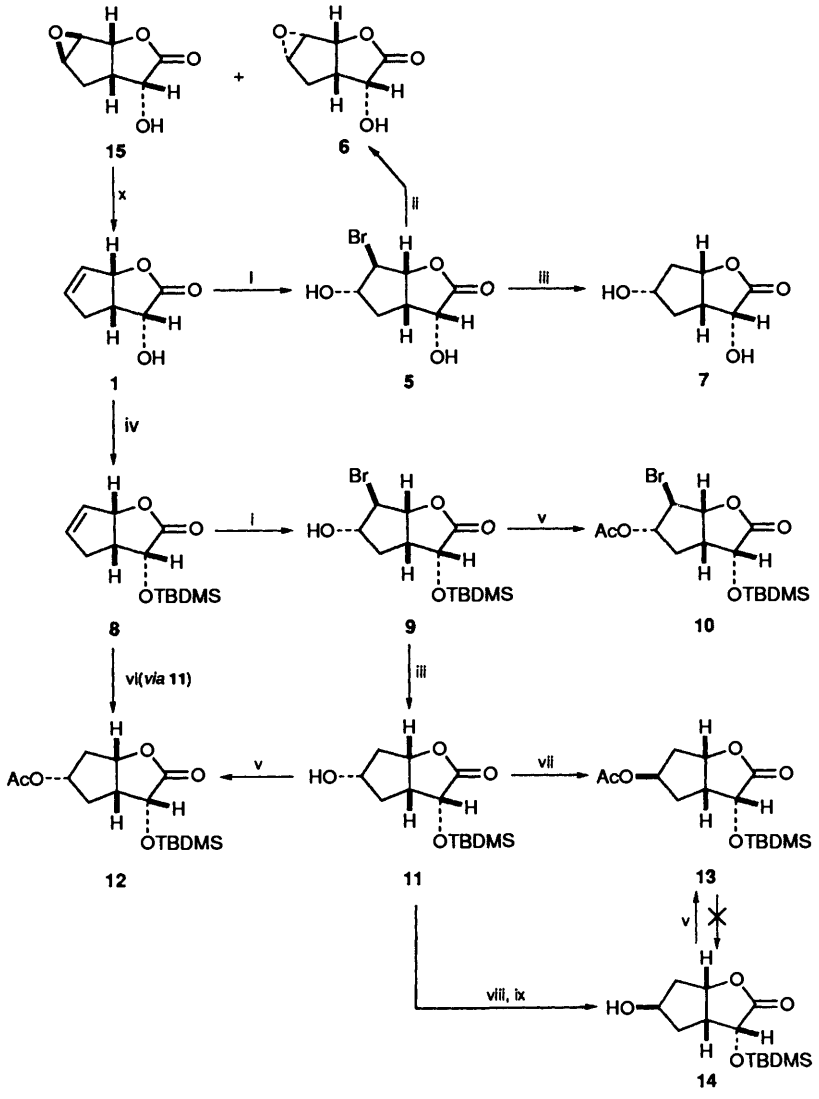
Finally in this series, epoxidation of compound **1** with *m*-chloroperbenzoic acid (MCPBA) furnished a mixture of the epoxides **6** and **15** in the ratio 2:11 and a total yield of 85%.

In general, the hydroxy lactone **3** was found to react with the electrophilic reagents under investigation less selectively than the epimeric lactone **1**. Thus, reaction of the lactone **3** with NBA in aq. acetone gave a mixture of the bromohydrins **16** and **17** in the ratio 2.5:1 (Scheme 2). Treatment of the separated bromohydrins **16** and **17** with potassium acetate in acetone gave the oxiranes **18** and **19**, respectively. The epoxides **18** and **19** were formed directly from the alkene **3** in the ratio 3:1 on treatment with MCPBA.

The silylated hydroxy lactone **20** reacted with NBA in aq. acetone to give, after acetylation, the bromo esters **21** and **22** in the ratio 2.3:1.

Somewhat surprisingly the corresponding reactions on the lactones **2** and **4** all conformed to the pattern set by the *exo*-hydroxy lactone **3**. Thus, the *endo*-hydroxy lactone **2** reacted *non-selectively* with NBA in aq. acetone to furnish the bromohydrins **23** and **24** in the ratio 2:1 (Scheme 3). Since NMR experiments could not give unequivocal structural assignments, X-ray crystal data on the diacetate **25** (derived from compound **24**) were obtained (Fig. 1). Diols **23** and **24** were independently converted into the corresponding epoxides **26** and **27** respectively using base, and X-ray data were obtained for the epoxides **26** and **27** (Figs. 2 and 3). The epoxides **26** and **27** were obtained in the ratio 1:3.4 on treatment of the lactone **2** with MCPBA. Treatment of the major compound formed in the latter reaction with hydroiodic acid gave the iodohydrin **28** as the only product. The iodohydrin **28** was further characterised by conversion into the diester **29**.

Silylation of the diol **23** gave mono- **30** and di-protected **31** species depending on the reaction conditions. The alcohol **30** was obtained as the major product when the silylated compound **32** was treated with HOBr under the standard conditions. The isomeric bromohydrin **33** was obtained as the minor product from the latter reaction (ratio **30**:**33** 3.3:1). Treatment



Scheme 1 *Reagents and conditions:* i, NBA, aq. acetone; ii, AcOK, acetone; iii, Bu_3SnH, AIBN, benzene, reflux; iv, TBDMS-Cl, imidazole, CH_2Cl_2; v, Ac_2O, DMAP, pyridine; vi, $Hg(OAc)_2$, aq. THF; then $NaBH_4$, THF, −60 °C; then v; vii, AcOH, Ph_3P, DEAD, THF; viii, $ClCH_2CO_2H$, Ph_3P, DEAD, THF; ix, $(NH_2)_2CS$, $NaHCO_3$, EtOH, reflux; x, MCPBA, TPB, $ClCH_2CH_2Cl$, 90 °C, sealed tube; then KF, CH_2Cl_2

of the fully protected material **31** with methoxide ion gave the oxirane **34**.[7]

Two bromohydrins **35** and **36** (ratio 2.2:1) were formed on reaction of the lactone **4** with hypobromous acid. The bromohydrin **35** was converted into the diacetate **37** [for which X-ray crystal data were obtained (Fig. 4)] and into the epoxides **38**, the minor product obtained on peracid oxidation of the parent lactone (Scheme 4). The major product obtained from the latter oxidation was the oxirane **39** (ratio **38**:**39** 1:2.4). Reaction of the silylated compound **40** with HOBr afforded a mixture of the bromohydrins **41** and **42** in the ratio 7:1.

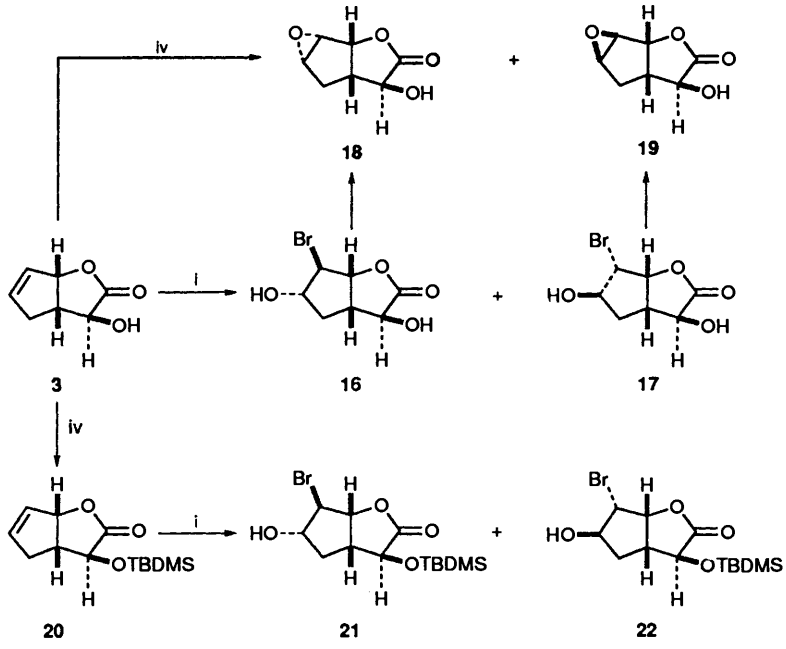
Discussion

In terms of target-orientated synthetic organic chemistry, compound **1** is a most attractive starting material. Simple derivation of the alkene unit occurs in a highly selective fashion to provide polyfunctional molecules having discrete and predictable substitution patterns. Compounds **2**–**4** are going to be less versatile synthons since the alkene unit is obviously much more open to attack from both faces.

Since the compounds **1**–**4** are fairly flexible, it is difficult to explain the above results by envisaging preferred conformations through which the substances invariably react with electrophiles. However, it does seem that the *endo*-hydroxyoxabicyclo[3.3.0]octenone **1** may prefer to react through conformation I, (Fig. 5) with the hydroxy group in a pseudo-equatorial arrangement, distant from the carbocyclic ring, and with the lactone moiety protecting the back-face of the alkene unit. Certainly we have seen no evidence of tricyclic compounds resulting from intramolecular nucleophilic attack by the pendant hydroxy group,[6] suggesting that the hydroxy group and the alkene unit are not adjacent. In addition there is no pronounced 'Henbest effect' on reaction of the unsaturated lactone **1** with peracid.

The *exo*-hydroxyoxabicyclo[3.3.0]octenone **3** is obviously able to accommodate conformations which lead to minor amounts of '*endo*'-bromo compounds and one transition state [II (Fig. 5)] displays an open arrangement which accommodates the hydroxy group in a pseudo-equatorial arrangement. The reaction of compound **3** with MCPBA tends to support the concept of an extended conformation since the major product is the *endo*-epoxide **18**, reflecting the preferred approach of the electrophile from the more substituted face of the carbocyclic ring. [It is noteworthy that formation of bromonium ion is reversible so that products are produced from the optimum arrangement of electrophile *and* attendant nucleophile].

The hydroxyoxabicyclo[4.3.0]nonenones **2** and **4** behave



Scheme 2 *Reagents and conditions:* i, NBA, aq. acetone; ii, AcOK, acetone; iii, TBDMS-Cl, imidazole, CH_2Cl_2; iv, MCPBA, TPB, $ClCH_2CH_2Cl$, 90 °C, sealed tube: then KF, CH_2Cl_2

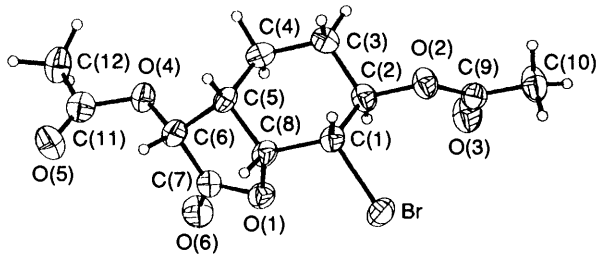


Fig. 1 X-Ray molecular structure of **25**

very similarly towards peracid and on bromination in hydroxylic solvent; conformations can be drawn (III and IV in Fig. 5) to explain the formation of the bromohydrins *via trans*-diaxial opening of the relevant bromonium ions. The conversion of epoxide **27** into the iodohydrin **28** obviously proceeds through a pathway similar to that described in diagram IV.

Further chemistry on this series of compounds, for example an approach to the natural product brefeldin from compound **1**, will be reported in due course.

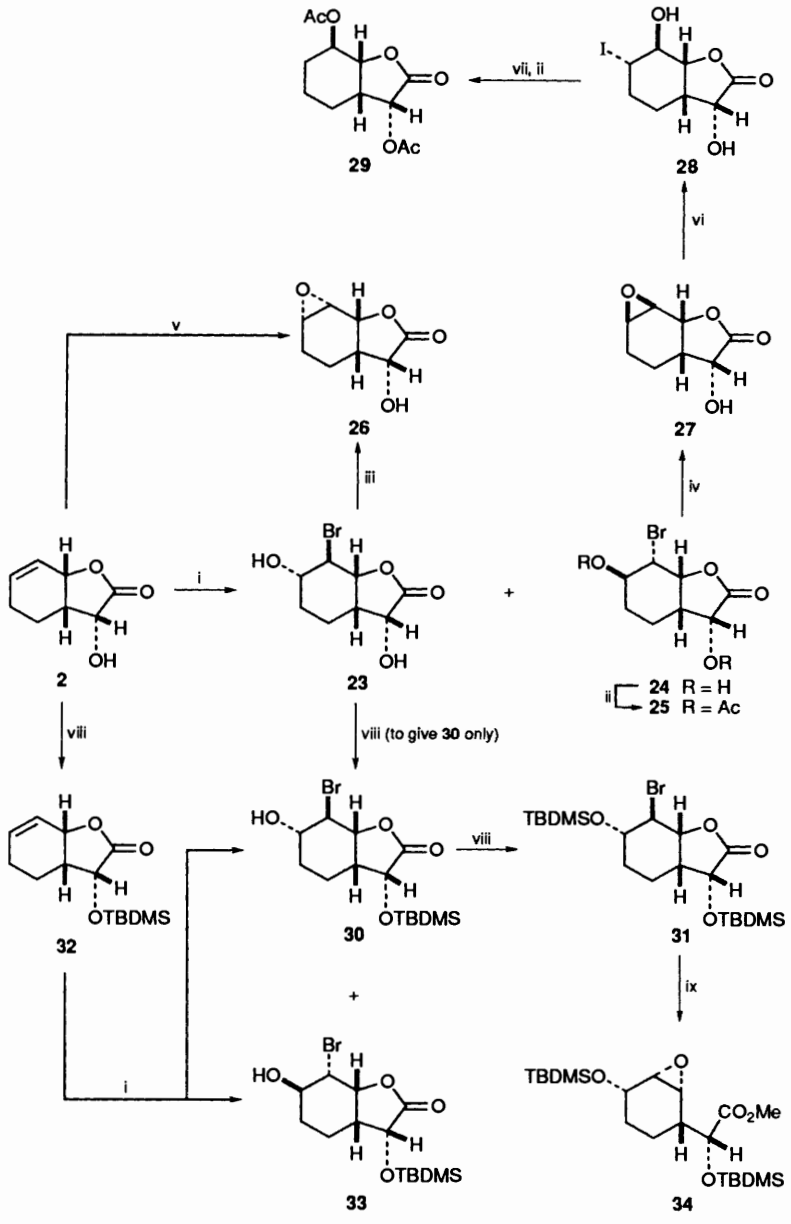
Experimental

Where necessary, solvents were dried and purified according to recommended procedures. Organic solutions were dried over magnesium sulfate, evaporation refers to removal of solvent on a rotary evaporator under reduced pressure. TLC was performed on precoated plates (Merck silica gel 60F 254). Chromatography refers to the method of Still *et al.*[8] using Merck Kieselgel, 60/230–400 mesh. Commercial MCPBA was dissolved in dichloromethane and the solution was dried over magnesium sulfate. The material obtained after filtration and subsequent evaporation was assumed to be of ~90% purity. Acetylation refers to a standard procedure on dissolution of the requisite alcohol in dry pyridine (10 cm^3 mequiv.$^{-1}$) containing acetic anhydride (4–5 mol equiv.) and 4-(dimethylamino)pyridine (cat.). After completion of the reaction (TLC), the volatile materials were evaporated off and the product was purified by chromatography.

M.p.s were measured on a Gallenkamp digital apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 881 spectrophotometer. NMR spectra were obtained on a Bruker AC 300 or AM 250 spectrometer. Coupling constants are given in Hz. The multiplicity indicated in the ^{13}C NMR spectra was determined by DEPT experiments. Mass determinations were obtained on a Kratos Profile HV-3 apparatus with the Impact Electronic technique, unless otherwise stated. Elemental analyses were performed by Butterworths Laboratories, Middlesex.

8-exo-*Bromo*-4-endo,7-endo-*dihydroxy*-2-*oxabicyclo*[3.3.0]-*octan*-3-*one* **5**.—NBA (108 mg, 0.78 mmol) was added in small portions to a solution of 4-*endo*-hydroxy-2-oxabicyclo-[3.3.0]oct-7-en-3-one **1** (100 mg, 0.71 mmol) in acetone (13 cm^3)–water (2 cm^3). The mixture was stirred overnight at room temperature, then was diluted with saturated aq. NaCl (10 cm^3) and extracted with ethyl acetate (6 × 5 cm^3). The organic layer was washed successively with 10% aq. sodium sulfite (0.5 cm^3) and brine. After drying of the solution, the solvent was evaporated off and the resulting residue was chromatographed (ethyl acetate–hexane, 7:3) to give the *title compound* **5** (152 mg, 90%) as a solid, m.p. 174 °C (from MeOH–EtOAc) (Found: C, 35.7; H, 3.7. $C_7H_9BrO_4$ requires C, 35.47; H, 3.83%); ν_{max}(KBr)/cm^{-1} 3420, 3005, 2954, 1767, 1200, 1148 and 1048; δ_H[250 MHz; $(CD_3)_2SO$] 5.90 (1 H, d, *J* 7.0, 4-OH), 5.44 (1 H, d, *J* 4.5, 7-OH), 4.93 (1 H, dd, *J* 6.7 and 1.5, 1-H), 4.54 (1 H, d, *J* 9.6, 4-H), 4.20 (1 H, dd, *J* 9.6 and 4.5, 7-H), 4.09 (1 H, m, 8-H), 3.16 (1 H, m, 5-H) and 2.1–1.8 (2 H, m, 6-H_2); δ_C[62.9 MHz; $(CD_3)_2SO$] 175.8 (C=O), 86.0 (CH), 78.2 (CH), 67.6 (CH), 57.7 (CH), 39.8 (CH) and 30.5 (CH_2); *m/z* 237 (M^+, weak), 139 (38%), 95 (51), 83 (59), 67 (100) and 57 (51).

7,8-endo-*Epoxy*-4-endo-*hydroxy*-2-*oxabicyclo*[3.3.0]*octan*-3-*one* **6**.—A mixture of compound **5** (237 mg, 1 mmol) and potassium acetate (118 mg, 1.2 mmol) in acetone (5 cm^3) was stirred for 24 h at room temperature under nitrogen. The solvent was evaporated off and the residue thus obtained was chromatographed (ethyl acetate–hexane, 7:3) to afford *compound* **6** (134 mg, 86%) as a solid, m.p. 118–120 °C (from EtOAc) (Found: C, 53.6; H, 4.6. $C_7H_8O_4$ requires C, 53.85; H, 5.16); ν_{max}(KBr)/cm^{-1} 3502, 1762, 1280, 1178, 1132 and 1022; δ_H(300 MHz; $CDCl_3$) 5.13 (1 H, dd, *J* 8.5 and 1.3, 1-H), 4.10 (1



Scheme 3 *Reagents and conditions:* i, NBA, aq. acetone; ii, Ac_2O, DMAP, pyridine; iii, AcOK, acetone; iv, Bu^{t}OK, THF; v, MCPBA, TPB, $ClCH_2CH_2Cl$, 90 °C, sealed tube; then KF, CH_2Cl_2; vi, HI, acetone, 0 °C; vii, Bu_3SnH, AIBN, benzene, reflux; viii, TBDMS-Cl, imidazole, CH_2Cl_2; ix, K_2CO_3, MeOH

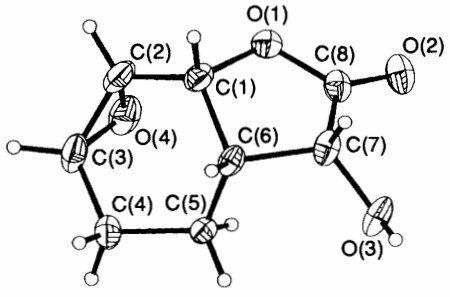


Fig. 2 X-Ray molecular structure of epoxide **26**

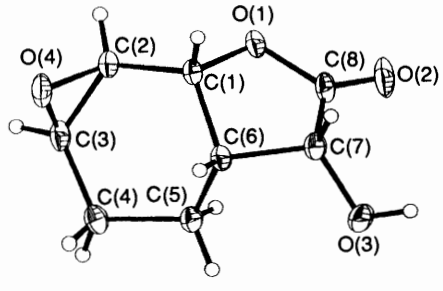
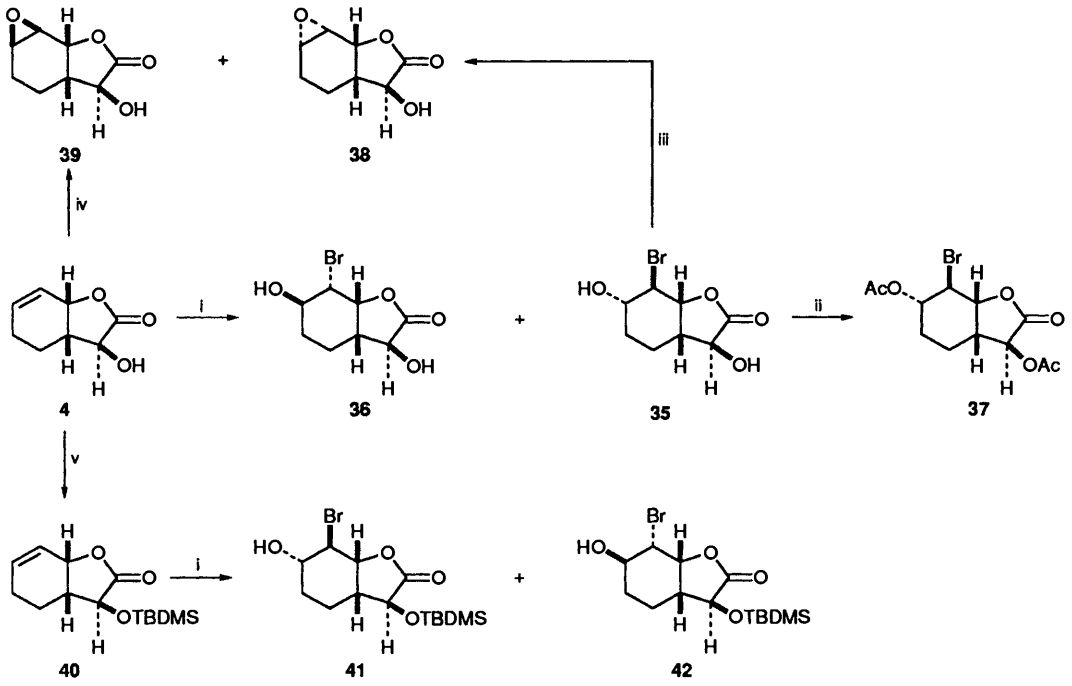


Fig. 3 X-Ray molecular structure of epoxide **27**

H, dd, *J* 12.1 and 10.1, 4-H), 3.71 (2 H, m, 7- and 8-H), 3.17 (1 H, d, *J* 12.1, OH), 2.94 (1 H, ddd, *J* 10.1, 9.5 and 8.5, 5-H), 2.55 (1 H, d, *J* 15.4, 6-H_{endo}) and 2.09 (1 H, ddd, *J* 15.4, 9.5 and 1.1, 6-H_{exo}); δ_C(62.9 MHz; $CDCl_3$) 176.1 (C=O), 82.6 (CH), 66.8 (CH), 59.7 (CH), 57.4 (CH), 36.8 (CH) and 26.0 (CH_2); *m/z* 156 (M^+, 17%), 111 (9), 97 (11), 81 (94), 66 (100) and 55 (81).

4-endo,7-endo-*Dihydroxy*-2-*oxabicyclo*[3.3.0]*octan*-3-*one* **7**.—A solution of bromohydrin **5** (100 mg, 0.42 mmol), AIBN (cat.) and tributyltin hydride (245 mg, 0.84 mmol) in dry benzene (13 cm^3) was stirred at reflux under nitrogen for 2 h. The solvent was removed under reduced pressure and the residue was partitioned between acetonitrile (10 cm^3) and



Scheme 4 *Reagents and conditions:* i, NBA, aq. acetone; ii, Ac_2O, DMAP, pyridine; iii, Bu^{t}OK, THF; iv, MCPBA, TPB, $ClCH_2CH_2Cl$, 90 °C, sealed tube; then KF, CH_2Cl_2; v, TBDMS-Cl, imidazole, CH_2Cl_2

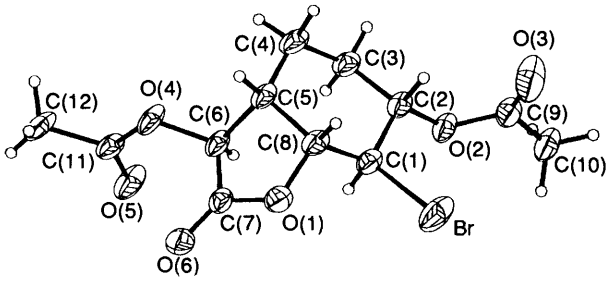


Fig. 4 X-Ray molecular structure of diacetate **37**

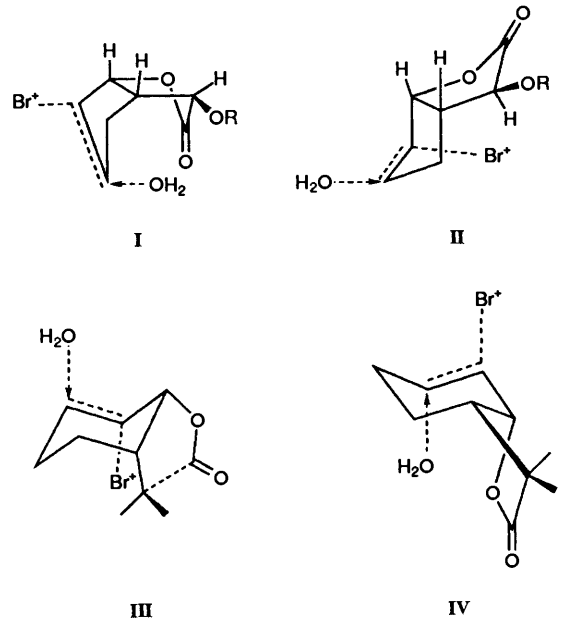


Fig. 5 Reaction modes for hydroxybromination of compounds **1**–**4** and silylated derivatives **8**, **20**, **32** and **40**

hexane (5 cm^3). The acetonitrile layer was separated and extracted with hexane (3 × 5 cm^3). The solvent was removed and the residue was purified by column chromatography (ethyl acetate–hexane, 4 : 1) to give the title compound **7** (62 mg, 93%) as an oil; ν_{max}(neat)/cm^{-1} 3372, 1766, 1197, 1136, 1083, 1067 and 1026; δ_H[250 MHz; $(CD_3)_2SO$] 5.58 (1 H, dd, *J* 6.9 and 0.9, 4-OH), 4.78 (1 H, t, *J* 6.0, 1-H), 4.69 (1 H, dd, *J* 3.8 and 0.9, 7-OH), 4.51 (1 H, ddd, *J* 9.3, 6.9 and 0.9, 4-H), 4.16 (1 H, m, 7-H), 2.90 (1 H, m, 5-H) and 2.12–1.70 (4 H, m, 6- and 8-H_2); δ_C[62.9 MHz; $(CD_3)_2SO$] 176.5 (C=O), 81.3 (CH), 71.4 (CH), 68.6 (CH), 41.9 (CH), 41.5 (CH_2) and 33.6 (CH_2).

4-endo-(tert-*Butyldimethylsiloxy*)-2-*oxabicyclo*[3.3.0]*oct*-7-*en*-3-*one* **8**.—Imidazole (2.72 g, 40 mmol) and *tert*-butyldimethylsilyl chloride (TBDMS-Cl) (3 g, 20 mmol) were added to a solution of compound **1** (1.4 g, 10 mmol) in anhydrous dichloromethane (30 cm^3) under nitrogen. After being stirred at room temperature for 1 h, the reaction mixture was poured onto saturated aq. NaCl (100 cm^3) and extracted with dichloromethane (3 × 20 cm^3). The combined extracts were dried and concentrated. Purification of the residue by column chromatography (ethyl acetate–hexane, 1 : 1) yielded *compound* **8** (2.3 g 90%) as a viscous oil which solidified on storage, m.p. 35–36 °C (Found: $[M + H]^+$, 255.1410. $C_{13}H_{22}O_3Si$ requires [M + H], 255.1416); ν_{max}(KBr)/cm^{-1} 3498, 2861, 1785, 1161, 1147 and 991; δ_H(250 MHz; $CDCl_3$) 6.20 (1 H, dt, *J* 5.5 and 2.2, 8-H), 5.90 (1 H, m, 7-H), 5.26 (1 H, dt, *J* 6.5 and 2.2, 1-H), 4.64 (1 H, d, *J* 9.5, 4-H) 3.10 (1 H, dddd, *J* 9.5, 9.5, 6.5 and 6.5, 5-H), 2.80 (1 H, dddd, *J* 18.5, 6.5, 2.2 and 2.2, 6-H), 2.38 (1 H, dddd, *J* 18.5, 9.5, 2.2 and 2.2, 6-H'), 0.95 (9 H, s, Bu^{t}Si), 0.10 (3 H, s, MeSi) and 0.08 (3 H, s, MeSi); δ_C(62.9 MHz; $CDCl_3$) 175.3 (C=O), 140.2 (CH), 128.0 (CH), 85.2 (CH), 69.9 (CH), 41.2 (CH), 31.3 (CH_2), 25.7 (3 × CH_3), 18.3 (C), −4.7 (CH_3) and −5.4 (CH_3).

8-exo-*Bromo*-4-endo-(tert-*butyldimethylsiloxy*)-7-endo-*hydroxy*-2-*oxabicyclo*[3.3.0]*octan*-3-*one* **9**.—By use of the procedure described for compound **5**, a mixture of compound **8** (300 mg, 1.18 mmol), NBA (193 mg, 1.40 mmol), acetone (5 cm^3) and water (1 cm^3) was stirred for 3 h. After the usual work-up, a residue was obtained, and purified by column chromatography (ethyl acetate–hexane, 1 : 7) to give *compound* **9** as a solid, m.p.

90.5–91.5 °C (from ethyl acetate–hexane) {Found: $[M + NH_4]^+$, (CI) 368.0893. $C_{13}H_{23}BrO_4Si$ requires $[M + NH_4]$, 368.0893}; ν_{max}(KBr)/cm^{-1} 3414, 2956, 1785, 1155, 1064 and 995; δ_H(250 MHz; $CDCl_3$) 5.20 (1 H, dt, *J* 6.8 and 1.0, 1-H), 4.56 (1 H, d, *J* 9.9, 4-H), 4.41 (1 H, m, 7-H), 4.25 (1 H, m, 8-H), 3.28 (1 H, dddd, *J* 9.9, 9.1, 6.8 and 4.2, 5-H), 2.47 (1 H, br s, OH), 2.40–2.20 (2 H, m, 6-H_2), 0.98 (9 H, s, Bu^{t}Si), 0.20 (3 H, s, MeSi) and 0.15 (3 H, s, MeSi); δ_C(62.9 MHz; $CDCl_3$) 174.5 (C=O), 87.2 (CH), 78.9 (CH), 69.2 (CH), 55.7 (CH), 40.9 (CH), 31.1 (CH_2), 25.7 (3 × CH_3), 18.3 (C), −4.6 (CH_3) and −5.3 (CH_3).

7-endo-*Acetoxy*-8-exo-*bromo*-4-endo-(tert-*butyldimethylsiloxy*)-2-*oxabicyclo*[3.3.0]*octan*-3-*one* **10**.—*Compound* **10** was obtained in 97% yield starting from compound **9** and by using the standard acetylation procedure. Purification was accomplished by column chromatography (ethyl acetate–hexane, 1:9). M.p. 83 °C (from ethyl acetate–hexane) (Found: $[M + H]^+$, 393.0735. $C_{15}H_{25}BrO_5Si$ requires [M + H], 393.0733); ν_{max}(KBr)/cm^{-1} 2861, 1795, 1732, 1375, 1241, 1136 and 940; δ_H(250 MHz; $CDCl_3$) 5.21 (1 H, m, 7-H), 5.05 (1 H, d, *J* 6.5, 1-H), 4.58 (1 H, d, *J* 10.0, 4-H), 4.37 (1 H, s, 8-H), 3.33 (1 H, m, 5-H), 2.45 (2 H, m, 6-H_2), 2.00 (3 H, s, Ac), 0.95 (9 H, s, Bu^{t}Si), 0.20 (3 H, s, MeSi) and 0.15 (3 H, s, MeSi); δ_C(62.9 MHz; $CDCl_3$) 174.2 (C=O), 169.7 (C=O), 86.0 (CH), 80.2 (CH), 69.0 (CH), 52.3 (CH), 40.6 (CH), 28.3 (CH_2), 25.6 (3 × CH_3), 20.7 (CH_3), 18.3 (C), −4.7 (CH_3) and −5.4 (CH_3).

4-endo-(tert-*Butyldimethylsiloxy*)-7-endo-*hydroxy*-2-*oxabicyclo*[3.3.0]*octan*-3-*one* **11**.—By use of a procedure similar to that described for compound **7**, a mixture of compound **9** (108 mg, 0.31 mmol), Bu_3SnH (182 mg, 0.62 mmol), AIBN (cat.) and dry benzene (9 cm^3) was refluxed for 1 h. Chromatographic purification (ethyl acetate–hexane, 4:1) gave compound **11** (76 mg, 91%) as a waxy solid, m.p. 91–92 °C; R_f 0.52 (ethyl acetate–hexane, 4:1); ν_{max}(KBr)/cm^{-1} 3459, 2933, 1780, 1167, 1007 and 973; δ_H(250 MHz; $CDCl_3$) 4.80 (1 H, t, *J* 6.0, 1-H), 4.51 (1 H, d, *J* 9.8, 4-H), 4.37 (1 H, m, 7-H), 3.01 (1 H, m, 5-H), 2.21–1.75 (5 H, m, 6- and 8-H_2, OH), 0.95 (9 H, s, Bu^{t}Si), 0.20 (3 H, s, MeSi) and 0.15 (3 H, s, MeSi); δ_C(62.9 MHz; $CDCl_3$) 175.2 (C=O), 82.2 (CH), 72.8 (CH), 70.2 (CH), 42.6 (CH), 42.5 (CH_2), 34.3 (CH_2), 25.6 (3 × CH_3), 18.3 (C), −4.6 (CH_3) and −5.3 (CH_3).

Alternatively, compound **11** was prepared in the following manner; mercury(II) acetate (0.319 g, 1 mmol) was dissolved in water (1 cm^3) and then tetrahydrofuran (THF) (1 cm^3) was added. After this mixture had been stirred for 15 min, compound **8** (0.254 g, 1 mmol) was added in one portion and the suspension was stirred for 24 h at room temperature. The solvent was evaporated off and the residual water was azeotropically distilled with toluene. The resulting oil was dissolved in dry THF (3 cm^3) and sodium borohydride (38 mg, 1 mmol) was added to the cooled solution (−60 °C) in small portions. After 4 h, glacial acetic acid (0.06 cm^3) was added and the solution was stirred for a further 30 min at −60 °C. The reaction mixture was allowed to warm to room temperature, then was filtered, and the volatiles were removed under reduced pressure. The residue so obtained was chromatographed to give pure compound **11** (95 mg, 35%).

7-endo-*Acetoxy*-4-endo-(tert-*butyldimethylsiloxy*)-2-*oxabicyclo*[3.3.0]*octan*-3-*one* **12**.—Acetylation of compound **11** was carried out by using the standard procedure. Purification by column chromatography (ethyl acetate–hexane, 1:4) gave *compound* **12** (92%) as a solid, m.p. 84 °C (from cyclohexane); R_f 0.16 (ethyl acetate–hexane, 1:4) (Found: C, 52.9; H, 8.1. $C_{15}H_{26}O_5Si$ requires C, 52.79; H, 8.33%); ν_{max}(KBr)/cm^{-1} 2960, 2936, 1771, 1732, 1253, 1071 and 858; δ_H(250 MHz; $CDCl_3$) 5.14 (1 H, m, 7-H), 4.95 (1 H, t, *J* 6.0, 1-H), 4.56 (1 H, d, *J* 10.0, 4-H), 3.05 (1 H, m, 5-H), 2.41 (1 H, ddd, *J* 15.1, 5.2 and 2.4, 6-H), 2.30 (1 H, m, 8-H), 2.05 (1 H, t, *J* 5.1, 8-H'), 1.94 (3 H, s, Me), 1.82 (1 H, m, 6-H'), 0.80 (9 H, s, Bu^{t}Si), 0.18 (3 H, s, MeSi) and 0.12 (3 H, s, MeSi); δ_C(62.9 MHz; $CDCl_3$) 175.1 (C=O), 170.6 (C=O), 81.5 (CH), 75.5 (CO), 69.6 (CH), 41.9 (CH), 40.1 (CH_2), 31.2 (CH_2), 25.6 (3 × CH_3), 21.1 (CH_3), 18.3 (C), −4.7 (CH_3) and −5.4 (CH_3); *m/z* 257 ($[M - C_4H_9]^+$, 11%), 197 (28), 153 (100), 131 (13), 117 (38), 75 (75), 67 (10) and 57 (30).

7-exo-*Acetoxy*-4-endo-(tert-*Butyldimethylsiloxy*)-2-*oxabicyclo*[3.3.0]*oxtan*-3-*one* **13**.—The alcohol **11** (57 mg, 0.21 mmol), triphenylphosphine (78 mg, 0.30 mmol) and chloroacetic acid (28 mg, 0.30 mmol) were dissolved in dry THF (3 cm^3). To this was added dropwise a solution of diethyl azodicarboxylate (DEAD) (52 mg, 0.30 mmol) in dry THF (1 cm^3) over a period of 5 min. The solution was stirred at room temperature for 2 h under nitrogen. The solvent was evaporated off under reduced pressure and the residue was taken up in diethyl ether (1 cm^3). Any insoluble material was filtered off and the solution was concentrated and chromatographed (ethyl acetate–hexane, 1:4) to give the *chloroacetate ester intermediate* as a solid (52 mg, 71%), m.p. 49.5–50.5 °C; R_f 0.25 (ethyl acetate–hexane, 1:4) (Found: $[M + H]^+$, 349.1228. $C_{15}H_{25}ClO_5Si$ requires [M + H], 349.1238); ν_{max}(KBr)/cm^{-1} 1790.

4-*endo*-(*tert*-Butyldimethylsiloxy)-7-*exo*-chloroacetoxy-2-oxabicyclo[3.3.0]octan-3-one (35 mg, 0.1 mmol) was treated with thiourea (11.4 mg, 0.15 mmol) and sodium hydrogen carbonate (12.6 mg, 0.15 mmol) in ethanol (10 cm^3) at reflux for 2 h. Evaporation of the solvent and subsequent chromatography (ethyl acetate–hexane, 1:1; R_f 0.19) gave the alcohol **14** (23 mg, 87%), which was in turn acetylated by a standard procedure to give the *title compound* **13** (25 mg, 94%) as an oil after chromatography (ethyl acetate–hexane, 3:7; R_f 0.31) (Found: $[M + H]^+$, 315.1636. $C_{15}H_{26}O_5Si$ requires [M + H], 315.1628); ν_{max}(neat)/cm^{-1} 2958, 2933, 1790, 1739, 1249, 1012 and 839; δ_H(250 MHz; $CDCl_3$) 5.26 (1 H, m, 7-H), 4.86 (1 H, dt, *J* 6.0 and 2.2, 4-H), 4.61 (1 H, d, *J* 8.2, 4-H), 3.12 (1 H, m, 5-H), 2.36 (1 H, ddd, *J* 16.0, 6.0 and 2.3, 8-H), 2.15 (2 H, m, 8-H', 6-H), 2.05 (3 H, s, Ac), 1.85 (1 H, m, 6-H'), 0.90 (9 H, s, Bu^{t}Si), 0.17 (3 H, s, MeSi) and 0.12 (3 H, s, MeSi); δ_C(62.9 MHz; $CDCl_3$), 175.0 (C=O), 170.1 (C=O), 80.5 (CH), 75.4 (CH), 70.7 (CH), 43.9 (CH), 40.4 (CH_2), 31.3 (CH_2), 25.6 (3 × CH_3), 21.1 (CH_3), 18.2 (C), −4.7 (CH_3) and −5.4 (CH_3).

Alternatively, compound **13** was prepared in the following manner: alcohol **11** (114 mg, 0.42 mmol), Ph_3P (156 mg, 0.60 mmol) and glacial acetic acid (0.036 cm^3, 0.60 mmol) were dissolved in dry THF (6 cm^3). To this was added dropwise a solution of DEAD (104 mg, 0.60 mmol) in dry THF (2 cm^3) over a period of 5 min. The solution was stirred at room temperature for 3 h under nitrogen. The solvent was evaporated off and the residue was taken up in diethyl ether (3 cm^3). Any insoluble material was filtered off and the solution was concentrated and chromatographed to give ester **13** (116 mg, 88%) as an oil.

7,8-exo-*Epoxy*-4-endo-*hydroxy*-2-*oxabicyclo*[3.3.0]*octan*-3-*one* **15**.—A tube charged with 4-*endo*-hydroxy-2-oxabicyclo-[3.3.0]oct-7-en-3-one **1** (100 mg, 0.71 mmol), 90% MCPBA (191 mg, 1 mmol), bis(5-*tert*-butyl-4-hydroxy-2-methylphenyl) sulfide[9] (TPB) (2 mg) and dry 1,2-dichloroethane (5 cm^3) was purged with nitrogen before sealing. The reaction mixture was then heated in an oil-bath at 90 °C for 1 h. After cooling, the clear solution was evaporated to dryness and the resulting residue was dissolved in dichloromethane (20 cm^3). Activated potassium fluoride (100 °C/0.1 mmHg; 1 h) (0.6 g) was added and the mixture was kept for 30 min before being filtered (in some cases this treatment was repeated in order to ensure the complete extraction of *m*-chlorobenzoic acid and unchanged MCPBA). Chromatography of the residue obtained after

evaporation (ethyl acetate–hexane, 3:2 as eluent) gave *compound* **15** (80 mg, 72%) as a solid, m.p. 82–83 °C (from EtOAc) (Found: C, 53.7; H, 5.0. $C_7H_8O_4$ requires C, 53.85; H, 5.16%); ν_{max}(KBr)/cm^{-1} 3370, 1780, 1404, 1170, 1134 and 1000; δ_H(300 MHz; $CDCl_3$) 4.88 (1 H, d, *J* 5.3, 1-H), 4.68 (1 H, d, *J* 8.5, 4-H), 3.90 (1 H, br s, OH), 3.72 (1 H, d, *J* 2.2, 8-H), 3.61 (1 H, s, 7-H), 2.86 (1 H, ddd, *J* 8.6, 7.9 and 5.3, 5-H), 2.15 (1 H, dd, *J* 15.4 and 8.6, 6-H_{exo}) and 1.96 (1 H, ddd, *J* 15.4, 7.9 and 1.3, 6-H_{endo}); δ_C(62.9 MHz; $CDCl_3$) 176.6 (C=O), 80.1 (CH), 68.9 (CH), 58.2 (CH), 56.5 (CH), 39.3 (CH) and 25.7 (CH_2); *m/z* 157 ([M + H]$^+$, 11%), 111 (71), 94 (45), 81 (91), 66 (62) and 55 (100). Further elution gave 7,8-*endo*-epoxy-4-*endo*-hydroxy-2-oxabicyclo[3.3.0]octan-3-one **6** (15 mg, 13%).

8-exo-*Bromo*-4-exo,7,endo-*dihydroxy*-2-*oxabicyclo*[3.3.0]-*octan*-3-*one* **16** *and* 8-endo-*Bromo*-4-exo,7-exo-*dihydroxy*-2-*oxabicyclo*[3.3.0]*octan*-3-*one* **17**.—NBA (118 mg, 0.85 mmol) was added portionwise to a stirred solution of compound **3** (100 mg, 0.71 mmol) in acetone (5 cm^3)–water (1 cm^3). The resulting mixture was stirred overnight at room temperature. After evaporation of the solvent, the residue was chromatographed (ethyl acetate–hexane, 7:3) to yield *compound* **16** (105 mg, 62%) as an oil (Found: [M]$^+$, 235.9685. $C_7H_9BrO_4$ requires [M], 235.9684); ν_{max}(neat)/cm^{-1} 3418, 2954, 1774, 1079, 1045 and 1010; δ_H[250 MHz; $(CD_3)_2SO$] 6.15 (1 H, br s, OH), 5.60 (1 H, br s, OH), 5.08 (1 H, dd, *J* 8.0 and 1.8, 1-H), 4.19 (3 H, m, 4-, 7- and 8-H), 2.84 (1 H, m, 5-H), 2.40 (1 H, m, 6-H) and 1.83 (1 H, m, 6-H′); δ_C[62.9 MHz; $(CD_3)_2SO$] 176.5 (C=O), 87.1 (CH), 77.0 (CH), 73.9 (CH), 56.5 (CH), 44.6 (CH) and 36.2 (CH_2).

Further elution yielded *compound* **17** (40 mg, 24%) as a solid, m.p. 122 °C (from EtOAc) (Found: [M]$^+$, 235.9678); ν_{max}(KBr)/cm^{-1} 3376, 1765, 1191, 1052 and 1023; δ_H[250 MHz; $(CD_3)_2SO$] 6.09 (1 H, d, *J* 1.2, 7-OH), 5.51 (1 H, d, *J* 5.0, 4-OH), 5.05 (1 H, dd, *J* 7.5 and 5.0, 4-H), 4.15 (3 H, m, 1-, 7- and 8-H), 2.79 (1 H, m, 5-H) and 1.94 (2 H, m, 6-H_2); δ_C[62.9 MHz; $(CD_3)_2SO$] 176.5 (C=O), 80.9 (CH), 75.7 (CH), 74.1 (CH), 56.9 (CH), 43.3 (CH) and 34.9 (CH_2).

7,8-endo-*Epoxy*-4-exo-*hydroxy*-2-*oxabicyclo*[3.3.0]*octan*-3-*one* **18**.—A mixture of bromohydrin **16** (237 mg, 1 mmol) and potassium acetate (118 mg, 1.2 mmol) in acetone (5 cm^3) was stirred for 24 h at room temperature under nitrogen. The solvent was evaporated off and the residue so obtained was chromatographed (ethyl acetate–hexane, 7:3) to afford the *title compound* **18** (78 mg, 50%) as a solid, m.p. 69–71 °C (Found: C, 53.4; H, 4.9. $C_7H_8O_4$ requires C, 53.85; H, 5.16%); ν_{max}(KBr)/cm^{-1} 3442, 1772, 1188, 1100 and 1020; δ_H(300 MHz; $CDCl_3$) 5.02 (1 H, dd, *J* 8.8 and 1.5, 1-H), 4.28 (1 H, d, *J* 7.7, 4-H), 3.92 (1 H, br s, OH), 3.65 (1 H, br s, 7-H), 3.61 (1 H, m, 8-H), 2.77 (1 H, ddd, *J* 9.9, 8.8 and 7.7, 5-H), 2.34 (1 H, dd, *J* 15.2 and 0.9, 6-H_{endo}) and 2.12 (1 H, ddd, *J* 15.2, 9.9 and 1.3, 6-H_{exo}); δ_C(62.9 MHz; $CDCl_3$) 178.2 (C=O), 81.7 (CH), 73.7 (CH), 59.2 (CH), 56.5 (CH), 42.5 (CH) and 30.7 (CH_2); *m/z* 157 ([M + H]$^+$, weak), 149 (12%), 111 (35), 93 (23), 83 (70), 66 (100) and 57 (79).

7,8-exo-*Epoxy*-4-exo-*hydroxy*-2-*oxabicyclo*[3.3.0]*octan*-3-*one* **19**.—A mixture of bromohydrin **17** (237 mg, 1 mmol) and potassium acetate (118 mg, 1.2 mmol) in acetone (5 cm^3) was stirred for 24 h at room temperature under nitrogen. The solvent was evaporated off and the residue so obtained was chromatographed (ethyl acetate–hexane, 7:3) to afford the *title compound* **19** (72 mg, 46%) as a solid, m.p. 142–144 °C (from EtOAc–MeOH) (Found: [M]$^+$, 156.0420. $C_7H_8O_4$ requires [M], 156.0422); ν_{max}(KBr)/cm^{-1} 3382, 1766, 1736, 1194, 1168 and 1006; δ_H[300 MHz; $(CD_3)_2SO$] 6.34 (1 H, d, *J* 5.5, OH), 5.04 (1 H, d. *J* 5.4, 1-H), 3.98 (1 H, d, *J* 5.5, 4-H), 3.76 (1 H, d, *J* 2.4, 8-H), 3.64 (1 H, m, 7-H), 2.34 (1 H, ddd, *J* 9.0, 5.4 and 0.9, 5-H), 2.30 (1 H, dd, *J* 18.6 and 9.0, 6-H_{exo}) and 1.52 (1 H, m, 6-H_{endo}); δ_C[62.9 MHz; $(CD_3)_2SO$] 175.8 (C=O), 81.7 (CH), 71.6 (CH), 57.0 (CH), 55.7 (CH), 43.0 (CH) and 28.9 (CH_2).

Compounds **18** and **19** were also obtained by direct epoxidation of 4-*exo*-hydroxy-2-oxabicyclo[3.3.0]oct-7-en-3-one **3** in 64 and 20% yield, respectively, by a procedure identical with that described for compounds **6** and **15**.

4-exo-(tert-*Butyldimethylsiloxy*)-2-*oxabicyclo*[3.3.0]*oct*-7-*en*-3-*one* **20**.—Imidazole (300 mg, 4.48 mmol) and TBDMS-Cl (340 mg, 2.24 mmol) were added to a solution of compound **3** (157 mg, 1.12 mmol) in anhydrous dichloromethane (3 cm^3) under nitrogen. After being stirred at room temperature for 1 h, the reaction mixture was poured onto saturated aq. NaCl (10 cm^3) and extracted with dichloromethane (3 × 3 cm^3), and the combined extracts were dried and concentrated. Purification by column chromatography (ethyl acetate–hexane, 1:9) yielded *compound* **20** (253 mg, 89%) as an oil; R_f 0.25 (ethyl acetate–hexane, 1:9) (Found: [M]$^+$, 254.1310. $C_{13}H_{22}O_3Si$ requires [M], 254.1338); ν_{max}(neat)/cm^{-1} 2933, 2861, 1784, 1254, 1145 and 992; δ_H(250 MHz; $CDCl_3$) 6.04 (1 H, m, 8-H), 5.88 (1 H, m, 7-H), 5.44 (1 H, m, 1-H), 4.06 (1 H, d, *J* 6.5, 4-H), 2.93 (1 H, m, 5-H), 2.72 (1 H, m, 6-H), 2.42 (1 H, m, 6-H′), 0.90 (9 H, s, Bu^{t}Si), 0.15 (3 H, s, MeSi) and 0.12 (3 H, s, MeSi); δ_C(62.9 MHz; $CDCl_3$) 175.7 (C=O), 136.3 (CH), 129.9 (CH), 86.3 (CH), 75.4 (CH), 45.5 (CH), 36.4 (CH_2), 25.6 (3 × CH_3), 18.1 (C), −4.5 (CH_3) and −5.1 (CH_3).

8-exo-*Bromo*-4-exo-(tert-*butyldimethylsiloxy*)-7-endo-*hydroxy*-2-*oxabicyclo*[3.3.0]*octan*-3-*one* **21** *and* 8-endo-*Bromo*-4-exo-(tert-*butyldimethylsiloxy*)-7-exo-*hydroxy*-2-*oxabicyclo*-[3.3.0]*octan*-2-*one* **22**.—NBA (60 mg, 0.43 mmol) was added in portions to a solution of compound **20** (100 mg, 0.39 mmol) in acetone (3 cm^3)–water (0.5 cm^3). The mixture was stirred for 24 h at room temperature, then was diluted with saturated aq. NaCl (3 cm^3) and extracted with ethyl acetate (3 × 4 cm^3). The organic layer was washed successively with 10% aq. sodium sulfite (0.5 cm^3) and brine. After drying of the mixture, the solvent was evaporated off and the resulting residue was chromatographed (ethyl acetate–hexane, 1:4) to give *compound* **21** (85 mg, 61%) as an oil, R_f 0.20 (ethyl acetate–hexane, 1:4) (Found: [M + H]$^+$, 351.0637. $C_{13}H_{23}BrO_4Si$ requires [M + H], 351.0627); ν_{max}(neat)/cm^{-1} 3393, 2959, 1774, 1362, 1256, 1099 and 839; δ_H(250 MHz; $CDCl_3$) 5.22 (1 H, d, *J* 7.4, 4-H), 4.68 (1 H, br s, OH), 4.43 (1 H, m, 7-H), 4.32 (1 H, d, *J* 2.4, 1-H), 4.24 (1 H, br s, 8-H), 2.98 (1 H, m, 5-H), 2.62 (1 H, ddd, *J* 14.1, 10.2 and 4.1, 6-H_{exo}), 1.95 (1 H, m, 6-H_{endo}), 0.80 (9 H, s, Bu^{t}Si), 0.17 (3 H, s, MeSi) and 0.16 (3 H, s, MeSi); δ_C(62.9 MHz; $CDCl_3$) 176.3 (C=O), 88.8 (CH), 78.6 (CH), 76.3 (CH), 54.5 (CH), 46.7 (CH), 36.4 (CH_2), 25.6 (3 × CH_3), 18.1 (C), −4.7 (CH_3) and −5.1 (CH_3).

Further elution gave the *bromohydrin* **22** (38 mg, 27%) as an oil, R_f 0.10 (ethyl acetate–hexane, 1:4) (Found: [M]$^+$, 350.0556. $C_{13}H_{23}BrO_4Si$ requires [M], 350.0549); ν_{max}(neat)/cm^{-1} 3417, 2932, 1781, 1465, 1256, 1110 and 839; δ_H(250 MHz; $CDCl_3$) 5.13 (1 H, ddd, *J* 7.5, 4.7 and 0.5, 1-H), 4.39 (1 H, m, 7-H), 4.20 (1 H, d, *J* 4.0, 4-H), 4.13 (1 H, dd, *J* 6.0 and 4.7, 8-H), 2.94 (1 H, m, 5-H), 2.45 (1 H, br s, OH), 2.14 (2 H, m, 6-H_2), 0.91 (9 H, s, Bu^{t}Si), 0.16 (3 H, s, MeSi) and 0.14 (3 H, s, MeSi)- δ_C(62.9 MHz; $CDCl_3$) 169.4 (C=O), 81.6 (CH), 76.3 (CH), 55.6 (CH), 44.6 (CH), 34.6 (CH), 31.2 (CH_2), 25.6 (3 × CH_3), 18.1 (C), −4.7 (CH_3) and −5.2 (CH_3).

5-exo-*Bromo*-4-endo,9-endo-*dihydroxy*-7-*oxabicyclo*-[4.3.0]*nonan*-8-*one* **23** *and* 5-endo-*Bromo*-4-exo,9-endo-*dihydroxy*-7-*oxabicyclo*[4.3.0]*nonan*-8-*one* **24**.—NBA (182 mg, 1.32 mmol) was added in portions to a solution of 9-*endo*-hydroxy-

7-oxabicyclo[4.3.0]non-4-en-8-one **2** (169 mg, 1.1 mmol) in acetone (20 cm^3)–water (3 cm^3). The mixture was stirred for 18 h at room temperature, then was diluted with saturated aq. NaCl (25 cm^3) and extracted with ethyl acetate (6 × 5 cm^3). The organic layer was washed successively with 10% aq. sodium sulfite (0.5 cm^3) and brine. After the mixture had been dried, the solvent was evaporated off and the resulting residue was chromatographed (ethyl acetate–hexane, 7:3) to give *compound* **23** (160 mg, 58%) as an oil, R_f 0.44 (EtOAc) (Found: C, 38.0; H, 4.4. $C_8H_{11}BrO_4$ requires C, 38.40; H, 4.43%); ν_{max}(neat)/cm^{-1} 3417, 2945, 1785, 1440, 1327, 1167, 1072 and 963; δ_H[250 MHz; $(CD_3)_2SO$] 5.10–3.70 (2 H, br, 4- and 9-OH), 4.71 (1 H, t, *J* 5.8, 6-H), 4.36 (1 H, d, *J* 6.5, 9-H), 4.17 (1 H, t, *J* 6.1, 5-H), 3.76 (1 H, m, 4-H), 2.62 (1 H, m, 1-H) and 1.92–1.48 (4 H, m, 2- and 3-H_2); δ_C[62.9 MHz; $(CD_3)_2SO$] 175.9 (C=O), 79.8 (CH), 70.1 (CH), 68.7 (CH), 55.9 (CH), 37.7 (CH), 27.9 (CH_2) and 16.3 (CH_2); *m/z* 251 ($[M]^+$, weak), 153 (17%), 127 (50), 109 (92), 91 (42), 81 (100), 67 (64) and 55 (76).

Further elution gave *bromohydrin* **24** (83 mg, 30%) as a solid, m.p. 187–188 °C (Found: C, 38.3; H, 4.2%); δ_H[250 MHz; $(CD_3)_2SO$] 5.90 (1 H, br s, OH), 5.25 (1 H, br s, OH), 4.68 (1 H, t, *J* 3.2, 6-H), 4.63 (1 H, d, *J* 9-H), 4.16 (1 H, dd, *J* 10.5 and 3.2, 5-H), 3.49 (1 H, dt, *J* 10.5 and 4.5, 4-H), 2.60 (1 H, m, 1-H), 1.91 (1 H, m, 3-H_{exo}), 1.70 (1 H, m, 3-H_{endo}), 1.32 (1 H, m, 2-H_{exo}) and 1.12 (1 H, m, 2-H_{endo}); δ_C[62.9 MHz; $(CD_3)_2SO$] 175.9 (C=O), 78.2 (CH), 71.8 (CH), 69.0 (CH), 57.0 (CH), 41.6 (CH), 32.6 (CH_2) and 20.0 (CH_2); *m/z* 251 (M^+, weak), 153 (42%), 125 (32), 109 (69), 91 (49), 83 (100), 67 (56) and 55 (68).

4-exo-,9-endo-*Diacetoxy*-5-endo-*bromo*-7-*oxabicyclo*[4.3.0]*nonan*-8-*one* **25**.—Compound **25** was obtained starting from compound **24** by using the standard acetylation procedure. Purification was accomplished by column chromatography (ethyl acetate–hexane, 1:1) to give *compound* **25**, as a solid, in 91% yield, m.p. 202–204 °C (from EtOAc) (Found: C, 42.2; H, 4.3. $C_{12}H_{15}BrO_6$ requires C, 43.01; H, 4.51%); ν_{max}(KBr)/cm^{-1} 3450, 2950, 1799, 1754, 1732, 1231 and 1054; δ_H(250 MHz; $CDCl_3$) 5.57 (1 H, d, *J* 6.2, 9-H), 5.05 (1 H, ddd, *J* 11.0, 10.8 and 4.2, 4-H), 4.78 (1 H, dd, *J* 3.6 and 3.5, 6-H), 4.06 (1 H, dd, *J* 10.8 and 3.5, 5-H), 2.89 (1 H, dddd, *J* 11.7, 6.2, 6.0 and 3.6, 1-H), 2.19 (1 H, m, 3-H_{exo}), 2.18 (3 H, s, Me), 2.10 (3 H, s, Me), 1.79 (1 H, m, 2-H_{exo}) and 1.61–1.34 (2 H, m, 2- and 3-H_{endo}); δ_C(62.9 MHz; $CDCl_3$) 170.1 (C=O), 169.6 (C=O), 169.5 (C=O), 78.0 (CH), 72.8 (CH), 71.2 (CH), 49.0 (CH), 40.1 (CH), 29.3 (CH_2), 20.6 (CH_3), 20.3 (CH_3) and 19.7 (CH_2); *m/z* 335 (M^+, weak), 153 (17%), 126 (14), 109 (100), 79 (66) and 51 (21).

4,5-endo-*Epoxy*-9-endo-*hydroxy*-7-*oxabicyclo*[4.3.0]*nonan*-8-*one* **26**.—A mixture of compound **23** (251 mg, 1 mmol) and potassium acetate (118 mg, 1.2 mmol) in acetone (5 cm^3) was refluxed for 30 h under nitrogen. The solvent was evaporated off and the residue so obtained was chromatographed (ethyl acetate as eluent) to afford compound **26** (124 mg, 73%) as a solid, m.p. 168–169 °C; R_f 0.25 (EtOAc) (Found: C, 56.5; H, 5.9. $C_8H_{10}O_4$ requires C, 56.47; H, 5.92%); ν_{max}(KBr)/cm^{-1} 3439, 2928, 1764, 1211, 1162 and 969; δ_H[300 MHz; $(CD_3)_2SO$] 5.81 (1 H, d, *J* 6.2, OH), 4.81 (1 H, dd, *J* 6.0 and 4.0, 6-H), 4.57 (1 H, dd, *J* 8.1 and 6.2, 9-H), 3.37 (2 H, m, 4- and 5-H), 2.33 (1 H, dddd, *J* 13.5, 8.1, 6.0 and 4.8, 1-H), 2.05 (1 H, dddd, *J* 15.0, 3.8, 2.7 and 2.6, 3-H_{endo}), 1.68 (1 H, dddd, *J* 15.0, 12.8, 4.2 and 0.7, 3-H_{exo}), 1.31 (1 H, dddd, *J* 13.7, 4.8, 4.2 and 2.7, 2-H_{exo}) and 1.07 (1 H, dddd, *J* 13.7, 13.5, 12.8 and 3.8, 2-H_{endo}); δ_C[62.9 MHz; $(CD_3)_2SO$] 176.4 (C=O), 71.8 (CH), 68.5 (CH), 52.1 (CH), 48.4 (CH), 37.4 (CH), 21.8 (CH_2) and 13.9 (CH_2); *m/z* 170 (M^+, weak), 107 (14%), 98 (53), 80 (100), 70 (57), 67 (39) and 57 (55).

4,5-exo-*Epoxy*-9-endo-*hydroxy*-7-*oxabicyclo*[4.3.0]*nonan*-8-*one* **27**.—A mixture of compound **24** (251 mg, 1 mmol) and potassium *tert*-butoxide (123 mg, 1.1 mmol) in dry THF (5 cm^3) was stirred for 36 h at room temperature under nitrogen. The solvent was evaporated off and the residue was chromatographed (EtOAc) to give the *title compound* **27** (104 mg, 61%) as a solid, m.p. 139 °C (from ethyl acetate–hexane) (Found: C, 56.1; H, 5.7. $C_8H_{10}O_4$ requires C, 56.47; H, 5.92%); ν_{max}(KBr)/cm^{-1} 3412, 2930, 1770, 1256, 1213, 1181, 1141 and 993; δ_H[300 MHz; $(CD_3)_2SO$] 5.95 (1 H, d, *J* 6.0, OH), 4.76 (1 H, dd, *J* 4.6 and 1.4, 6-H), 4.59 (1 H, dd, *J* 6.3 and 6.0, 9-H), 3.36 (1 H, dd, *J* 5.3 and 4.1, 4-H), 3.30 (1 H, dd, *J* 4.1 and 1.4, 5-H), 2.35 (1 H, dddd, *J* 12.6, 6.3, 4.6 and 4.1, 1-H), 2.09 (1 H, m, 3-H_{endo}), 1.58–1.42 (2 H, m, 2- and 3-H_{exo}) and 0.87 (1 H, m, 2-H_{endo}); δ_C[62.9 MHz; $(CD_3)_2SO$] 175.9 (C=O), 71.0 (CH), 69.9 (CH), 52.5 (CH), 49.6 (CH), 36.7 (CH), 21.2 (CH_2) and 16.1 (CH_2); *m/z* 170 (M^+, weak), 125 (46%), 107 (70), 98 (95), 79 (85), 70 (83) and 55 (100).

Compounds **26** and **27** were also prepared by direct epoxidation of 9-*endo*-hydroxy-7-oxabicyclo[4.3.0]non-4-en-8-one **2** in 18 and 61% yield, respectively, by a procedure similar to that described for compounds **6** and **15**, after reaction for 3 h.

5-exo,9-endo-*Dihydroxy*-4-endo-*iodo*-7-*oxabicyclo*[4.3.0]*nonan*-8-*one* **28**.—Hydriodic acid (55% solution of hydrogen iodide in water; 0.1 cm^3, 0.73 mmol) was added to a stirred solution of epoxy alcohol **27** (95 mg, 0.56 mmol) in acetone (4 cm^3) at 0 °C. The mixture was stirred for 30 min after which time 5% aq. sodium hydrogen carbonate (0.5 cm^3) and 10% aq. sodium hydrogen sulfite (0.5 cm^3) were added. The solvent was evaporated off and the residual water was azeotroped with toluene. The resulting residue was chromatographed (ethyl acetate–hexane, 3:2) to afford the *iodohydrin* **28** (120 mg, 72%) as a solid, m.p. 152 °C; R_f 0.20 (ethyl acetate–hexane, 7:3) (Found: $[M]^+$, 297.9801. $C_8H_{11}IO_4$ requires [M], 297.9702); ν_{max}(KBr)/cm^{-1} 3350, 2856, 1770, 1183, 1077 and 1009; δ_H[250 MHz; $(CD_3)_2SO$] 6.12 (1 H, d, *J* 5.5, OH), 5.89 (1 H, d, *J* 5.5, OH), 4.25 (3 H, m, 5-, 6- and 9-H), 3.93 (1 H, m, 4-H), 2.63 (1 H, m, 1-H), 2.05 (2 H, m, 3-H_2) and 1.57 (2 H, m, 2-H_2); δ_C[62.9 MHz; $(CD_3)_2SO$] 176.2 (C=O), 79.0 (CH), 72.2 (CH), 70.0 (CH), 37.6 (CH), 32.6 (CH), 31.0 (CH_2) and 20.4 (CH_2).

5-exo,9-endo-*Diacetoxy*-7-*oxabicyclo*[4.3.0]*nonan*-8-*one* **29**.—A solution of iodohydrin **28** (55 mg, 0.18 mmol), AIBN (cat.) and tributyltin hydride (105 mg, 0.36 mmol) in dry benzene (7 cm^3) was stirred at reflux under nitrogen for 90 min. The solvent was removed under reduced pressure and the residue was partitioned between acetonitrile (7 cm^3) and hexane (4 cm^3). The acetonitrile layer was separated and extracted with hexane (3 × 3 cm^3). The solvent was removed and the residue was purified by column chromatography (ethyl acetate–hexane, 4:1) to obtain 5-*exo*,9-*endo*-dihydroxy-7-oxabicyclo[4.3.0]-nonan-8-one (30 mg, 94%), which was converted into the *diacetyl derivative* **29** by means of the standard acetylation procedure. Purification was achieved by chromatography (ethyl acetate–hexane, 2:3, R_f 0.34) (Found: C, 56.2; H, 6.5. $C_{12}H_{16}O_6$ requires C, 56.25; H, 6.29%); ν_{max}(KBr)/cm^{-1} 2931, 2867, 1812, 1744, 1370, 1247, 1218 and 1028; δ_H(250 MHz; $CDCl_3$) 5.50 (1 H, d, *J* 6.7, 9-H), 5.22 (1 H, m, 5-H), 4.35 (1 H, t, *J* 4.0, 6-H), 2.87 (1 H, m, 1-H), 1.88–1.12 (6 H, m, 2-, 3- and 4-H_2), 2.17 (3 H, s, Me) and 2.05 (3 H, s, Me); δ_C(62.9 MHz; $CDCl_3$) 171.5 (C=O), 169.6 (C=O), 169.5 (C=O), 74.0 (CH), 72.4 (CH), 67.0 (CH), 36.5 (CH), 25.0 (CH_2), 20.9 (CH_3), 20.6 (CH_2), 20.3 (CH_3) and 16.7 (CH_2); *m/z* 256 (M^+, weak), 196 (17%), 140 (14), 126 (28), 110 (100), 98 (26), 83 (28) and 81 (76).

5-exo-*Bromo*-9-endo-(tert-*butyldimethylsiloxy*)-4-endo-*hydroxy*-7-*oxabicyclo*[4.3.0]*nonan*-8-*one* **30**.—Imidazole (184 mg, 2.70 mmol) and TBDMS-Cl (203 mg, 1.35 mmol) were added to a solution of compound **23** (340 mg, 1.35 mmol) in anhydrous

dichloromethane (15 cm^3) under nitrogen. After being stirred at room temperature for 1 h, the reaction mixture was poured onto saturated aq. NaCl (30 cm^3) and extracted with dichloromethane (5 × 10 cm^3), and the combined extracts were dried and concentrated. Purification was effected by column chromatography (ethyl acetate–hexane, 3:7) to yield *compound* **30** (450 mg, 91%) as a solid, m.p. 165–166 °C; R_f 0.36 (ethyl acetate–hexane, 3:7) (Found: C, 46.0; H, 7.1. $C_{14}H_{25}BrO_4Si$ requires C, 46.03; H, 6.90%); ν_{max}(KBr)/cm^{-1} 3443, 2931, 1780, 1259, 1192, 1158 and 966; δ_H(250 MHz; $CDCl_3$) 4.65 (1 H, t, *J* 6.0, 6-H), 4.38 (1 H, d, *J* 6.5, 9-H), 4.23 (1 H, t, *J* 6.2, 5-H), 3.94 (1 H, m, 4-H), 2.67 (1 H, m, 1-H), 2.25 (1 H, br s, OH), 2.06 (1 H, m, 3-H), 1.80 (3 H, m, 3-H′ and 4-H_2), 0.90 (9 H, s, Bu^{t}Si), 0.18 (3 H, s, MeSi) and 0.16 (3 H, br s, MeSi); δ_C(62.9 MHz; $CDCl_3$) 171.9 (C=O), 80.1 (CH), 72.2 (CH), 70.4 (CH), 54.4 (CH), 38.8 (CH), 27.0 (CH_2), 25.7 (CH_2), 25.6 (3 × CH_3), 16.8 (C), −4.7 (CH_3) and −5.2 (CH_3); *m/z* 364 (M^+, weak), 227 (22%), 209 (47), 131 (37), 81 (38), 75 (100) and 57 (29).

5-exo-*Bromo*-4-endo,9-endo-*bis*-(tert-*butyldimethylsiloxy*)-7-*oxabicyclo*[4.3.0]*nonan*-8-*one* **31**.—Compound **31** was obtained by following a similar procedure as described for compound **30** using an excess of TBDMS-Cl (3 mol equiv.) and imidazole (6 mol equiv.). Chromatographic purification (ethyl acetate–hexane, 1:20) gave *compound* **31** in 90% yield as a solid, m.p. 71–72 °C (from hexane); R_f 0.33 (ethyl acetate–hexane, 1:20) (Found: $[M]^+$, 478.1590. $C_{20}H_{39}BrO_4Si_2$ requires [M], 478.1570); ν_{max}(KBr)/cm^{-1} 2933, 2860, 1799, 1156, 1020 and 976; δ_H(250 MHz; $CDCl_3$) 4.59 (1 H, t, *J* 3.9, 6-H), 4.44 (1 H, d, *J* 6.5, 9-H), 4.22 (1 H, t, *J* 3.5, 5-H), 4.08 (1 H, m, 4-H), 2.71 (1 H, m, 1-H), 2.05 (1 H, m, 3-H), 1.85–1.45 (3 H, m, 2-H_2 and 3-H′), 0.93 (9 H, s, Bu^{t}Si), 0.89 (9 H, s, Bu^{t}Si), 0.19 (3 H, s, MeSi), 0.15 (3 H, s, MeSi), 0.11 (3 H, s, MeSi) and 0.05 (3 H, s, MeSi); δ_C(62.9 MHz; $CDCl_3$) 174.2 (C=O), 77.3 (CH), 72.9 (CH), 70.0 (CH), 49.6 (CH), 37.6 (CH), 25.8 (CH_2), 25.7 (3 × CH_3), 25.6 (3 × CH_3), 18.3 (C), 17.9 (C), 15.2 (CH_2), −4.7 (CH_3), −4.8 (CH_3), −5.0 (CH_3) and −5.3 (CH_3).

9-endo-(tert-*Butyldimethylsiloxy*)-7-*oxabicyclo*[4.3.0]*non*-4-*en*-8-*one* **32**.—Imidazole (2.72 g, 40 mmol) and TBDMS-Cl (3 g, 20 mmol) were added to a solution of compound **2** (1.54 g, 10 mmol) in anhydrous dichloromethane (30 cm^3) under nitrogen. After being stirred at room temperature for 1 h, the reaction mixture was poured onto saturated aq. NaCl (100 cm^3) and extracted with dichloromethane (3 × 20 cm^3). The combined extracts were dried and concentrated. Column chromatographic purification (ethyl acetate–hexane, 1:4) yielded *compound* **32** (2.5 g, 93%) as a solid, m.p. 51 °C (from hexane); R_f 0.55 (ethyl acetate–hexane, 1:4) (Found: C, 62.7; H, 9.15. $C_{14}H_{24}O_3Si$ requires C, 62.64; H, 9.01%); ν_{max}(KBr)/cm^{-1} 2958, 2934, 1789, 1254, 1027 and 990; δ_H(250 MHz; $CDCl_3$) 6.20 (1 H, m, 4-H), 5.90 (1 H, m, 5-H), 4.64 (1 H, d, *J* 7.5, 9-H), 4.58 (1 H, m, 6-H), 2.54 (1 H, m, 1-H), 2.20 (1 H, m, 3-H), 2.00 (2 H, m, 2-H and 3-H′), 1.24 (1 H, m, 2-H′), 0.92 (9 H, s, Bu^{t}Si), 0.20 (3 H, s, MeSi) and 0.16 (3 H, s, MeSi); δ_C(62.9 MHz; $CDCl_3$) 175.1 (C=O), 136.0 (CH), 122.2 (CH), 72.3 (CH), 70.6 (CH), 39.9 (CH), 25.7 (3 × CH_3), 23.4 (CH_2), 18.3 (C), 17.8 (CH_2), −4.6 (CH_3) and −5.4 (CH_3); *m/z* 269 ($[M + H]^+$, weak), 211 (19%), 167 (100), 149 (15), 132 (17) and 75 (58).

5-endo-*Bromo*-9-endo-(tert-*butyldimethylsiloxy*)-4-exo-*hydroxy*-7-*oxabicyclo*[4.3.0]*nonan*-8-*one* **33**.—NBA (207 mg, 1.5 mmol) was added in small portions to a solution of compound **32** (270 mg, 1 mmol) in acetone (13 cm^3–water (2 cm^3). The mixture was stirred for 24 h at room temperature, then was diluted with saturated aq. NaCl (10 cm^3) and extracted with ethyl acetate (3 × 5 cm^3). The organic layer was washed successively with 10% aq. sodium sulfite (0.5 cm^3) and brine. After drying of the solution the solvent was evaporated off and the resulting residue was chromatographed (ethyl acetate–hexane, 3:7) to give compound **30** (215 mg, 59%). Further elution gave *bromohydrin* **33** (66 mg, 18%) as a solid, m.p. 158–159 °C; R_f 0.27 (ethyl acetate–hexane, 3:7) (Found: $[M + H]^+$, 365.0794. $C_{14}H_{25}BrO_4Si$ requires [M + H], 365.0784); ν_{max}(KBr)/cm^{-1} 3433, 2934, 1778, 1255, 1166 and 1065; δ_H(250 MHz; $CDCl_3$) 4.63 (1 H, t, *J* 3.5, 6-H), 4.57 (1 H, d, *J* 6.2, 9-H), 3.97 (1 H, dd, *J* 10.0 and 3.5, 5-H), 3.87 (1 H, m, 4-H), 2.60 (1 H, m, 1-H), 2.50 (1 H, d, *J* 2.4, OH), 2.18 (1 H, m, 3-H), 1.90 (1 H, m, 2-H), 1.42 (2 H, m, 2- and 3-H′), 0.90 (9 H, s, Bu^{t}Si), 0.19 (3 H, s, MeSi) and 0.13 (3 H, s, MeSi); δ_C(62.9 MHz; $CDCl_3$) 174.0 (C=O), 77.5 (CH), 73.8 (CH), 70.0 (CH), 57.7 (CH), 42.7 (CH), 31.1 (CH_2), 25.6 (3 × CH_3), 20.2 (CH_2), 18.2 (C), −4.7 (CH_3) and −5.4 (CH_3).

Methyl 2-(tert-*Butyldimethylsiloxy*)-2-{5-(tert-*butyldimethylsiloxy*)-7-*oxabicyclo*[4.1.0]*heptan*-2-*yl*}*acetate* **34**.—A mixture of compound **31** (73 mg, 0.15 mmol) and potassium carbonate (21 mg, 15 mmol) in dry methanol (3 cm^3) was stirred for 24 h at room temperature under nitrogen. The solvent was evaporated off and the residue so obtained was chromatographed (ethyl acetate–hexane, 1:4) to afford *compound* **34** (43 mg, 66%) as an oil; R_f 0.33 (benzene) (Found: C, 58.2; H, 9.55. $C_{21}H_{42}O_5Si_2$ requires C, 58.56; H, 9.83%); ν_{max}(neat)/cm^{-1} 2956, 2934, 1753, 1255, 1154, 1100, 1021 and 838; δ_H(250 MHz; $CDCl_3$) 4.26 (1 H, d, *J* 10.0, C*H*CO_2Me), 4.05 (1 H, m, 5-H), 3.72 (3 H, s, CO_2Me), 3.36 (1 H, t, *J* 3.5, 1-H), 3.23 (1 H, dd, *J* 3.9 and 2.5, 6-H), 2.19 (1 H, m, 2-H), 1.70–1.08 (4 H, m, 3- and 4-H_2), 0.92 (9 H, s, Bu^{t}Si), 0.90 (9 H, s, Bu^{t}Si), 0.18 (3 H, s, MeSi), 0.13 (3 H, s, MeSi), 0.09 (3 H, s, MeSi) and 0.08 (3 H, s, MeSi); δ_C(62.9 MHz; $CDCl_3$) 173.3 (C=O), 73.9 (CH), 68.5 (CH), 56.4 (CH), 54.2 (CH), 51.6 (CH_3), 37.4 (CH), 27.4 (CH_2), 25.9 (3 × CH_3), 25.6 (3 × CH_3), 20.2 (CH_2), 18.2 (C), 18.1 (C), −4.6 (2 × CH_3), −5.3 (CH_3) and −5.4 (CH_3); *m/z* 430 (M^+, weak), 373 (26%), 281 (36), 241 (42), 209 (27), 147 (47), 115 (36), 85 (82), 73 (100) and 59 (55).

5-endo-*Bromo*-4-exo,9-exo-*dihydroxy*-7-*oxabicyclo*[4.3.0]-*nonan*-8-*one* **36** *and* 5-exo-*Bromo*-4-endo,9-exo-*dihydroxy*-7-*oxabicyclo*[4.3.0]*nonan*-8-*one* **35**.—NBA (138 mg, 1 mmol) was added portionwise to a solution of 9-*exo*-hydroxy-7-oxabicyclo[4.3.0]non-4-en-8-one **4** (130 mg, 0.84 mmol) in acetone (15 cm^3)–water (1 cm^3). The mixture was stirred for 24 h at room temperature, then was diluted with saturated aq. NaCl (5 cm^3) and extracted with ethyl acetate (6 × 5 cm^3). The organic layer was washed successively with 10% aq. sodium sulfite (0.5 cm^3) and brine. After the solution had been dried, the solvent was removed and the resulting residue was chromatographed (MeOH–Et_2O, 1:24) to obtain *compound* **36** (61 mg, 29%) as a solid, m.p. 191–193 °C; R_f 0.31 (MeOH–Et_2O, 1:24) (Found: C, 39.0; H, 4.4. $C_8H_{11}BrO_4$ requires C, 38.40; H, 4.43%); ν_{max}(KBr)/cm^{-1} 2946, 1764, 1454, 1193, 1066 and 938; δ_H[250 MHz; $(CD_3)_2SO$] 6.31 (1 H, d, *J* 5.0, 9-OH), 5.33 (1 H, d, *J* 5.5, 4-OH), 4.96 (1 H, t, *J* 4.0, 6-H), 4.28 (1 H, dd, *J* 9.5 and 4.0, 5-H), 3.95 (1 H, dd, *J* 5.0 and 2.2, 9-H), 3.60 (1 H, m, 4-H), 2.40 (1 H, m, 1-H), 1.89 (1 H, m, 3-H_{exo}), 1.75 (1 H, m, 2-H_{exo}), 1.35 (1 H, m, 3-H_{endo}) and 1.09 (1 H, m, 2-H_{endo}); δ_C[62.9 MHz; $(CD_3)_2SO$] 175.2 (C=O), 80.6 (CH), 73.2 (CH), 68.5 (CH), 57.2 (CH), 43.1 (CH), 31.1 (CH_2) and 21.0 (CH_2); *m/z* 251 (M^+, weak), 205 (20%), 167 (36), 149 (43), 125 (48), 109 (86), 95 (64), 83 (100), 67 (64) and 57 (86).

Further elution gave *bromohydrin* **35** (135 mg, 64%) as a solid, m.p. 180–181 °C; R_f 0.26 (MeOH–Et_2O, 1:24) (Found: C, 38.8; H, 4.3%); ν_{max}(KBr)/cm^{-1} 3438, 3358, 2934, 1771, 1141 and 1008; δ_H[250 MHz; $(CD_3)_2SO$] 5.85 (1 H, br s, OH), 5.22 (1 H, br s, OH), 4.66 (1 H, t, *J* 8.2, 6-H), 4.41 (1 H, d, *J* 12.5, 9-H), 4.05

(1 H, t, *J* 10.1, 5-H), 3.50 (1 H, dt, *J* 10.1 and 3.5, 4-H), 2.44 (1 H, m, 1-H) and 1.90–0.98 (4 H, m, 2- and 3-H_2); δ_C[62.9 MHz; $(CD_3)_2SO$] 176.1 (C=O), 80.7 (CH), 70.5 (CH), 66.3 (CH), 62.2 (CH), 43.6 (CH), 29.1 (CH_2) and 19.5 (CH_2); *m/z* 251 (M^+, weak), 167 (5%), 149 (16), 109 (24), 83 (100) and 57 (26).

4-endo,9-exo-*Diacetoxy*-5-exo-*bromo*-7-*oxabicyclo*[4.3.0]-*nonan*-8-*one* **37**.—*Compound* **37** was obtained in 94% yield, starting from compound **35** by using the standard acetylation procedure. Purification was accomplished by column chromatography (ethyl acetate–hexane, 2:3). M.p. 153–155 °C (Found: C, 42.4; H, 4.4; Br, 24.2. $C_{12}H_{15}BrO_6$ requires C, 43.00; H, 4.51; Br, 23.84%); ν_{max}(KBr)/cm^{-1} 4582, 2949, 1812, 1747, 1382, 1226 and 1017; δ_H(300 MHz; C_6D_6) 5.26 (1 H, d, *J* 11.7, 9-H), 4.63 (1 H, ddd, *J* 10.7, 10.7 and 4.0, 4-H), 3.98 (1 H, dd, *J* 9.2 and 7.7, 6-H), 3.09 (1 H, dd, *J* 10.7 and 9.2, 5-H), 1.93 (1 H, ddddd, *J* 11.7, 7.7, 5.5, 2.7 and 0.7, 1-H), 1.72 (3 H, s, 9-OAc), 1.63 (3 H, s, 4-OAc), 1.53 (1 H, ddddd, *J* 13.5, 4.2, 4.0, 2.7 and 0.7, 3-H_{exo}), 1.24 (1 H, dddd, *J* 14.8, 3.8, 2.7 and 2.7, 2-H_{endo}), 1.07 (1 H, dddd, *J* 13.5, 13.1, 10.7 and 3.8, 3-H_{endo}) and 0.79 (1 H, dddd, *J* 14.8, 13.1, 5.5 and 4.2, 2-H_{exo}); δ_C(62.9 MHz; (C_6D_6) 170.2 (C=O), 169.2 (C=O), 168.9 (C=O), 80.1 (CH), 71.8 (CH), 67.4 (CH), 53.3 (CH), 40.8 (CH), 25.6 (CH_2), 20.1 (CH_3), 19.6 (CH_3) and 19.1 (CH_2); *m/z* 335 (M^+, weak), 214 (9%), 188 (18), 153 (29), 118 (23), 109 (100) and 83 (98).

4,5-endo-*Epoxy*-9-exo-*hydroxy*-7-*oxabicyclo*[4.3.0]*nonan*-8-*one* **38**.—A mixture of compound **35** (251 mg, 1 mmol) and potassium *tert*-butoxide (123 mg, 1.1 mmol) in dry THF (5 cm^3) was stirred for 36 h at room temperature under nitrogen. The solvent was evaporated off and the residue was chromatographed (ethyl acetate–hexane, 4:1) to give the *epoxide* **38** (94 mg, 55%) as an oil, R_f 0.25 (ethyl acetate–hexane, 4:1) (Found: $[M + H]^+$, 171.0655. $C_8H_{10}O_4$ requires [M + H], 171.0657); ν_{max}(neat)/cm^{-1} 3423, 2865, 1779, 1121, 1087 and 997; δ_H(300 MHz; $CDCl_3$) 4.89 (1 H, dd, *J* 8.2 and 2.9, 6-H), 4.38 (1 H, d, *J* 8.6, 9-H), 3.95 (1 H, br s, OH), 3.42 (1 H, ddd, *J* 4.0, 3.6 and 1.5, 4-H), 3.36 (1 H, dd, *J* 4.0 and 2.9, 5-H), 2.51 (1 H, dddd, *J* 8.6, 8.2, 5.7 and 5.5, 1-H) and 2.10–1.56 (4 H, m, 2- and 3-H_2); δ_C(62.9 MHz; $CDCl_3$) 177.7 (C=O), 75.6 (CH), 69.7 (CH), 54.8 (CH), 51.3 (CH), 39.9 (CH), 19.4 (CH_2) and 19.2 (CH_2).

4,5-exo-*Epoxy*-9-exo-*hydroxy*-7-*oxabicyclo*[4.3.0]*nonan*-8-*one* **39**.—A mixture of 9-*exo*-hydroxy-7-oxabicyclo[4.3.0]non-4-en-8-one **4** (154 mg, 1 mmol), 90% MCPBA (267 mg, 1.4 mmol), TPB (2 mg) and dry 1,2-dichloroethane (8 cm^3) was heated for 2 h at 90 °C in a sealed tube and then worked-up in the same manner as described for compound **15**. The final residue was chromatographed (ethyl acetate–hexane, 4:1) to give *epoxide* **39** (95 mg, 56%) as an oil, R_f 0.36 (ethyl acetate–hexane, 4:1) (Found: $[M]^+$, 170.0585. $C_8H_{10}O_4$ requires [M], 170.0579); ν_{max}(neat)/cm^{-1} 3437, 2868, 1789, 1130 and 1011; δ_H(300 MHz; $CDCl_3$) 4.69 (1 H, dd, *J* 8.6 and 1.2, 6-H), 4.29 (1 H, d, *J* 11.0, 9-H), 3.23 (1 H, m, 4-H), 3.10 (1 H, d, *J* 3.5, 5-H), 2.65 (1 H, br s, OH), 2.50 (1 H, m, 1-H), 2.10 (2 H, m, 3-H_2) and 1.63 (2 H, m, 2-H_2); δ_H(62.9 MHz; $CDCl_3$) 177.7 (C=O), 71.8 (CH), 66.7 (CH), 52.3 (CH), 50.9 (CH), 37.9 (CH), 18.3 (CH_2) and 13.8 (CH_2).

Further elution gave epoxide **38** (40 mg, 23%).

9-exo-(tert-*Butyldimethylsiloxy*)-7-*oxabicyclo*[4.3.0]*non*-4-*en*-8-*one* **40**.—Imidazole (382 mg, 5.62 mmol) and TBDMS-Cl (433 mg, 2.87 mmol) were added to a solution of compound **4** (220 mg, 1.43 mmol) in anhydrous dichloromethane (5 cm^3) and the resulting mixture was stirred for 1 h under nitrogen. After work-up, the residue was purified by chromatography (ethyl acetate–hexane, 1:1) to afford *compound* **40** (355 mg, 93%) as an oil (Found: $[M + H]^+$, 269.1572. $C_{14}H_{24}O_3Si$ requires [M + H], 269.1573); ν_{max}(neat)/cm^{-1} 2935, 1789, 1325, 1255, 1145 and 998; δ_H(250 MHz; $CDCl_3$) 5.98 (1 H, ddt, *J* 10.0, 3.8 and 1.1, 4-H), 5.78 (1 H, ddd, *J* 10.0, 4.8 and 2.1, 5-H), 4.92 (1 H, m, 6-H), 4.16 (1 H, d, *J* 8.1, 9-H), 2.57 (1 H, m, 1-H), 2.11 (2 H, m, 3-H_2), 1.77 (2 H, m, 2-H_2), 0.90 (9 H, s, Bu^{t}Si), 0.18 (3 H, s, MeSi) and 0.15 (3 H, s, MeSi); δ_C(62.9 MHz; $CDCl_3$) 175.4 (C=O), 132.5 (CH), 124.5 (CH), 73.2 (CH), 70.5 (CH), 41.9 (CH), 25.6 (3 × CH_3), 20.9 (CH_2), 20.0 (CH_2), 10.1 (C), −4.5 (CH_3) and −5.2 (CH_3).

5-exo-*Bromo*-9-exo-(tert-*butyldimethylsiloxy*)-4-endo-*hydroxy*-7-*oxabicyclo*[4.3.0]*nonan*-8-*one* **41** *and* 5-endo-*Bromo*-9-exo-(tert-*butyldimethylsiloxy*)-4-exo-*hydroxy*-7-*oxabicyclo*-[4.3.0]*nonan*-8-*one* **42**.—NBA (204 mg, 1.48 mmol) was added in portions to a solution of compound **40** (305 mg, 1.14 mmol) in acetone (10 cm^3)–water (2 cm^3). After the mixture had been stirred for 24 h, and a usual work-up, a residue was obtained, which was chromatographed (ethyl acetate–hexane, 1:7) to afford *bromohydrin* **41** (320 mg, 77%) as a solid, m.p. 129 °C; R_f 0.25 (ethyl acetate–hexane, 3:7) (Found: C, 45.65; H, 6.9. $C_{14}H_{25}BrO_4Si$ requires C, 46.03; H, 6.90%); ν_{max}(KBr)/cm^{-1} 3443, 2935, 1778, 1253, 1151, 992 and 839; δ_C(250 MHz; $CDCl_3$) 4.86 (1 H, m, 6-H), 4.28 (1 H, d, *J* 11.5, 9-H), 3.71 (2 H, m, 4- and 5-H), 2.65 (1 H, m, 1-H), 2.55 (1 H, br s, OH), 2.14 (1 H, m, 3-H), 2.05 (1 H, m, 2-H), 1.75 (1 H, m, 2-H′), 1.52 (1 H, m, 3-H′), 0.90 (9 H, s, Bu^{t}Si), 0.19 (3 H, s, MeSi) and 0.15 (3 H, s, MeSi); δ_C(62.9 MHz; $CDCl_3$) 174.2 (C=O), 80.3 (CH), 71.7 (CH), 68.4 (CH), 61.0 (CH), 44.3 (CH), 27.4 (CH_2), 25.6 (3 × CH_3), 19.7 (CH_2), 18.2 (C), −4.4 (CH_3) and −5.2 (CH_3); *m/z* 365 ($[M + H]^+$, weak), 309 (13%), 227 (46), 209 (44), 183 (40), 139 (17), 131 (48), 79 (50), 75 (100) and 57 (37).

Further elution afforded *bromohydrin* **42** (47 mg, 11%) as a solid, m.p. 140–141 °C; R_f 0.13 (ethyl acetate–hexane, 3:7) (Found: C, 46.2; H, 7.0%); ν_{max}(KBr)/cm^{-1} 3475, 2930, 1775, 1321, 1213, 1104, 1093 and 937; δ_H(250 MHz; $CDCl_3$) 5.10 (1 H, t, *J* 3.4, 1-H), 4.05 (2 H, m, 5- and 9-H), 3.89 (1 H, dt, *J* 10.5 and 3.8, 4-H), 2.50 (1 H, br s, OH), 2.34 (1 H, m, 6-H), 2.15 (1 H, ddd, *J* 13.5, 7.5 and 3.8, 3-H), 1.82 (1 H, m, 2-H), 1.46 (1 H, m, 3-H′), 1.22 (1 H, m, 2-H′), 0.90 (9 H, s, Bu^{t}Si), 0.16 (3 H, s, MeSi) and 0.14 (3 H, s, MeSi); δ_C(62.9 MHz; $CDCl_3$) 173.6 (C=O), 81.1 (CH), 75.7 (CH), 69.4 (CH), 57.4 (CH), 45.1 (CH), 31.0 (CH_2), 25.6 (3 × CH_3), 21.4 (CH_2), 18.1 (C), −4.9 CH_3) and −5.3 (CH_3); *m/z* 365 ($[M + H]^+$, weak), 309 (43%), 281 (20), 247 (26), 209 (20), 183 (27), 131 (52), 109 (44), 91 (37), 81 (78), 75 (100) and 57 (29).

X-Ray Crystallography.—Crystals of compounds **25**, **26**, **27** and **37** suitable for X-ray work were grown from ethyl acetate. All crystallographic measurements were made at 298 K by using a Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating anode generator using Mo-Kα radiation (λ = 0.710 69 Å) by following procedures described elsewhere.[10] The structures were solved by direct methods (SHELX-S)[11] and refined by full-matrix least-squares (SHELXL-93)[12] using all unique F_o^2 data corrected for Lorentz and polarisation factors, and absorption effects (DIFFABS).[13] In all cases, the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined freely with individual U_{iso}-values in compounds **26** and **27**, but those in compounds **25** and **37** were included in calculated positions with the U_{iso}-values tied to the U_{eq}-values of the parent carbons; in compound **37**, an isotropic extinction parameter was also refined [final value = 0.38(2)]. Sources of scattering factors were as in ref. 12. The crystal data and details of data collection and structure refinement are presented in Table 1. The atomic coordinates, anisotropic displacement parameters of the non-

Table 1 Crystal data and details of data collection and refinement for compounds **25**–**27** and **37**

	25	**26**	**27**	**37**
Formula	$C_{12}H_{15}BrO_6$	$C_8H_{10}O_4$	$C_8H_{10}O_4$	$C_{12}H_{15}BrO_6$
M	335.15	170.16	170.16	335.15
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
a/Å	7.839(4)	10.370(1)	6.818(2)	7.977(1)
b/Å	18.130(2)	4.8833(8)	7.703(2)	9.477(2)
c/Å	9.771(1)	15.632(1)	8.128(2)	10.926(1)
α/°	90	90	66.01(1)	112.89(1)
β/°	93.10(2)	102.29(1)	84.27(3)	89.37(1)
γ/°	90	90	80.80(1)	112.29(1)
v/Å^3	1386.6(8)	773.4(2)	384.7(2)	695.0(2)
Space group	$2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	P-1 (No. 2)	P-1 (No. 2)
Z	4	4	2	2
D_c/g cm^{-3}	1.605	1.461	1.469	1.602
F(000)	680	360	180	340
μ/cm^{-1}	29.8	1.2	1.2	29.8
Crystal size/mm^3	0.25 × 0.20 × 0.12	0.35 × 0.28 × 0.15	0.35 × 0.20 × 0.15	0.22 × 0.15 × 0.08
θ-range for data/°	2.25–25.53	4.33–30.16	2.74–29.80	2.52–29.93
h_{min}, h_{max}	−6, 8	−13, 7	−9, 6	−11, 9
k_{min}, k_{max}	−13, 20	−6, 4	−10, 10	−12, 12
l_{min}, l_{max}	−10, 10	−20, 20	−10, 7	−15, 8
Total data measured	4564	3741	2050	3676
Total unique (R_{int})	2196 (0.113)	1928 (0.055)	1771 (0.046)	3171 (0.062)
Absorption correction factors (min, max)	0.753, 1.035	0.810, 1.125	0.898, 1.138	0.882, 1.355
No. of parameters/data	174/2196	149/1928	149/1771	175/3171
ρ_{min}, ρ_{max}/e Å^{-3}	−0.51, 0.66	−0.16, 0.12	−0.13, 0.16	−0.42, 0.28
R_1*	0.104 (0.062)**	0.066 (0.043.	0.060 (0.041)	0.105 (0.055)
wR_2*	0.173 (0.138)**	0.128 (0.100)	0.129 (0.099)	0.186 (0.142)

* $R_1 = \Sigma(F_o - F_c)/\Sigma(F_o)$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o)^2]$. ** R_1- and wR_2-values for data with $I > 2\sigma(I)$ are given in parentheses.

hydrogen atoms, and tables of bond lengths and angles have been deposited as supplementary material with the Cambridge Crystallographic Data Centre.*

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* For details of the system, see Instructions for Authors, in the January issue.

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