The Reactions of Norbornyl-type Cations derived from the Reaction of Silver Toluene-4-sulphonate with 3-Substituted 5-Iodonorbornane-2,6-lactones

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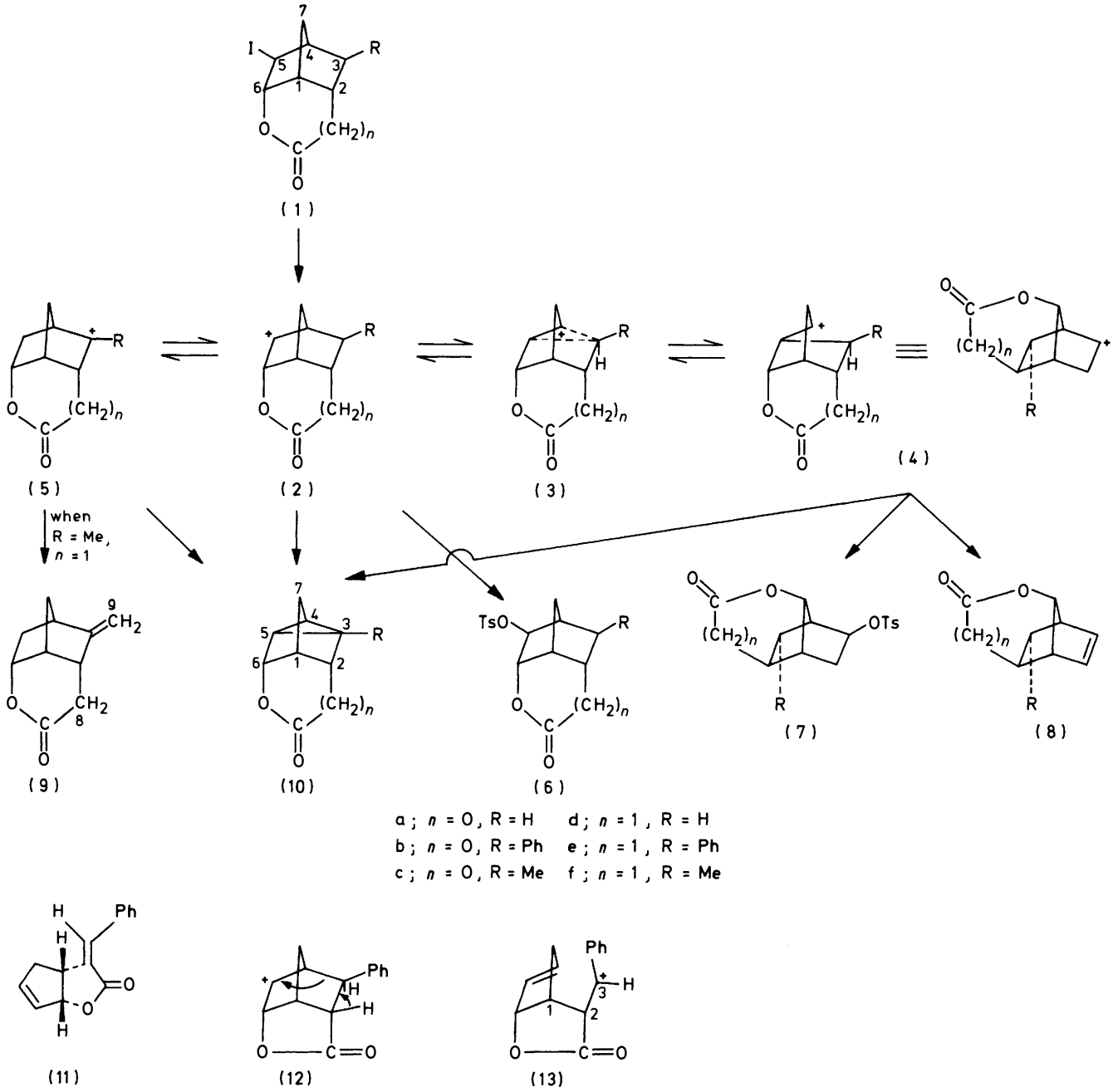
A series of 3-phenyl- and 3-methyl-substituted 6-*endo*-hydroxy-5-*exo*-iodonorborn-2-*endo*-ylcarboxylic acid γ-lactones and the corresponding acetic acid δ-lactones have been prepared, and their reaction with silver toluene-4-sulphonate studied in acetonitrile solution. In each case the products formed have been isolated and identified, and shown to be derived from the initially formed norobornyl-type cation or the cation derived from Wagner–Meerwein rearrangement. The normal reaction of these cations is capture by toluene-4-sulphonate anion, but in certain cases the cations lose a proton to give an unsaturated or nortricyclene lactone. 3-*exo*-Substituents reduce the extent of the Wagner–Meerwein rearrangement to a varying degree.

Some forty years ago Waters [1] commented that the mechanism for unimolecular dissociation is largely determined by the dielectric constant of the solvent medium and, that for the dissociation of carbon–halogen bonds into ions, solvents of dielectric constant >20 were desirable. With this in mind we have used acetonitrile (dielectric constant 38) as solvent in studies (Schemes 1 and 2) of norbornyl-type cations produced by reaction of norbornane iodolactones with silver toluene-4-sulphonate. In our initial studies [2] the sole product from 6-*endo*-hydroxy-5-*exo*-iodonorborn-2-*endo*-ylcarboxylic acid γ-lactone (1a) was 7-*syn*-hydroxy-3-*exo*-tosyloxynorborn-6-*exo*-ylcarboxylic acid γ-lactone (7a). Product formation is readily accommodated by a Wagner–Meerwein rearrangement of the initially formed norbornyl cation (2a) to give (4a), which is then captured by the toluene-4-sulphonate anion affording (7a). The reaction [3] of the corresponding 3-*exo*-phenyl-iodo-γ-lactone (2b) is very different in that the analogous Wagner–Meerwein rearrangement gives (7b) as a minor (9.1%) product only. The major products are the toluene-4-sulphonate (6b) (19.7%) and the unsaturated lactone (11) (70.9%), both of which are derived from the initially formed norbornyl-type cation (2b). It was suggested that this cation could be captured by a toluene-4-sulphonate anion to give (6b) or undergo the fragmentation depicted in (12) to give the unsaturated lactone (11). Although a synchronous fragmentation (12) of (2b) to give (11) was favoured,[3] a stepwise reaction involving an intermediate benzyl-type cation (13) was also a possibility. It was hoped that reaction of the 3-*endo*-phenyl-iodo-γ-lactone (14a) with silver toluene-4-sulphonate would distinguish between these possibilities since a concerted fragmentation of its derived norbornyl-type cation (15a) would give the *Z*-isomer of (11), whereas a stepwise fragmentation would permit the intermediate C-3 epimer of (13) to undergo rotation about its C-2, C-3 bond resulting in at least partial interconversion to (13) and hence formation of some (11). In the event neither (11) nor its *Z*-isomer were formed; the major product was the nortricyclene lactone (10b) and the toluene-4-sulphonate (18a). Thus for (14a), when the phenyl group is a 3-*endo*-substituent, Wagner–Meerwein rearrangement of the initially formed norbornyl cation (15a) occurs readily; both products (10b) and (18a) are derived from the rearranged cation (17a) by cyclisation and by toluene-4-sulphonate anion capture, respectively. In a further attempt to determine the effect of substituents on the propensity of cations (2) to rearrange, the reaction of the 3-*exo*-methyl-iodo-γ-lactone (1c) with silver toluene-4-sulphonate was examined and the toluene-4-sulphonates (6c) and (7c) derived from (2c) and (4c), respectively, were obtained as products in the ratio of 2.5 : 1. Once again the presence of a 3-*exo*-substituent has reduced the extent of the Wagner–Meerwein rearrangement of (2) ⟶ (4). This would appear to be consistent with the general observation [4–6] that 6-substituents reduce the rate of solvolysis of norborn-2-yl toluene-4-sulphonates since the intermediate norborn-2-yl cations are of reduced stability.

The reaction of 6-*endo*-hydroxy-5-*exo*-iodonorborn-2-*endo*-ylacetic acid δ-lactone (1d) is similar to that of (1a) in that Wagner–Meerwein rearrangement of the norbornyl cation (2d) occurs to give cation (4d) from which a major product (7d) is derived. The other major product is the nortricyclene lactone (10d) and its origin had been suggested [7] as involving the transition state (20) whereby silver ions aid the departure of the iodide ion, and at the same time the toluene-4-sulphonate anion assists in the loss of the 3-*endo*-hydrogen as a proton so that the electrons of the 3-*endo*-C–H bond displace iodide ion and effect cyclisation. However, attractive as such a proposal may be, it must now be considered unlikely as no similar reaction occurs with the iodo-γ-lactones (1a—c), and for the 3-*endo*-phenyl-iodo-γ-lactone (14a) which does give a nortricyclene lactone such a mechanism is not possible. In view of the ready rearrangement of (2a) to (4a) from which (7a) the sole product of reaction of (1a) is derived, it would seem most probable that (2d) also undergoes a similar rearrangement to give (4d) and that both the isolated products are derived from it. The formation of (10d) is shown in Scheme 3.

The 3-*exo*-phenyl (1e), 3-*endo*-phenyl (14b), and 3-*exo*-methyl (1f) iodo-γ-lactones each give rise to products derived from both the initially formed norbornyl-type cations (2e), (15b), and (2f) and the cations (4e), (17b), and (4f) derived from Wagner–Meerwein rearrangement. For the 3-*exo*-phenyl-iodo-δ-lactone (1e) the cations (2e) and (4e) are of comparable importance in product formation. Respective capture of these cations by toluene-4-sulphonate anion leads to (6e) and (7e). Alternatively, to capture by toluene-4-sulphonate anion, the cation (4e) to a small extent loses a proton giving the unsaturated lactone (8e). The 3-*endo*-phenyl-iodo-δ-lactone (14b) follows a quite different reaction pathway to that of its 3-*exo*-phenyl isomer (4e), but similar to that of the 3-*endo*-phenyl-iodo-γ-lactone (14a) in forming the nortricyclene lactone (10e) as major product; the ether (19a) is an additional but less important product. The nortricyclene lactone (10e) cannot be formed directly from (15b) and will have its origin, by analogy with (10b), in the Wagner–Meerwein rearrangement cation, which in this case is (17b). This further supports the route in Scheme 3 for the formation of the unsubstituted nortricyclene lactone (10d) derived from

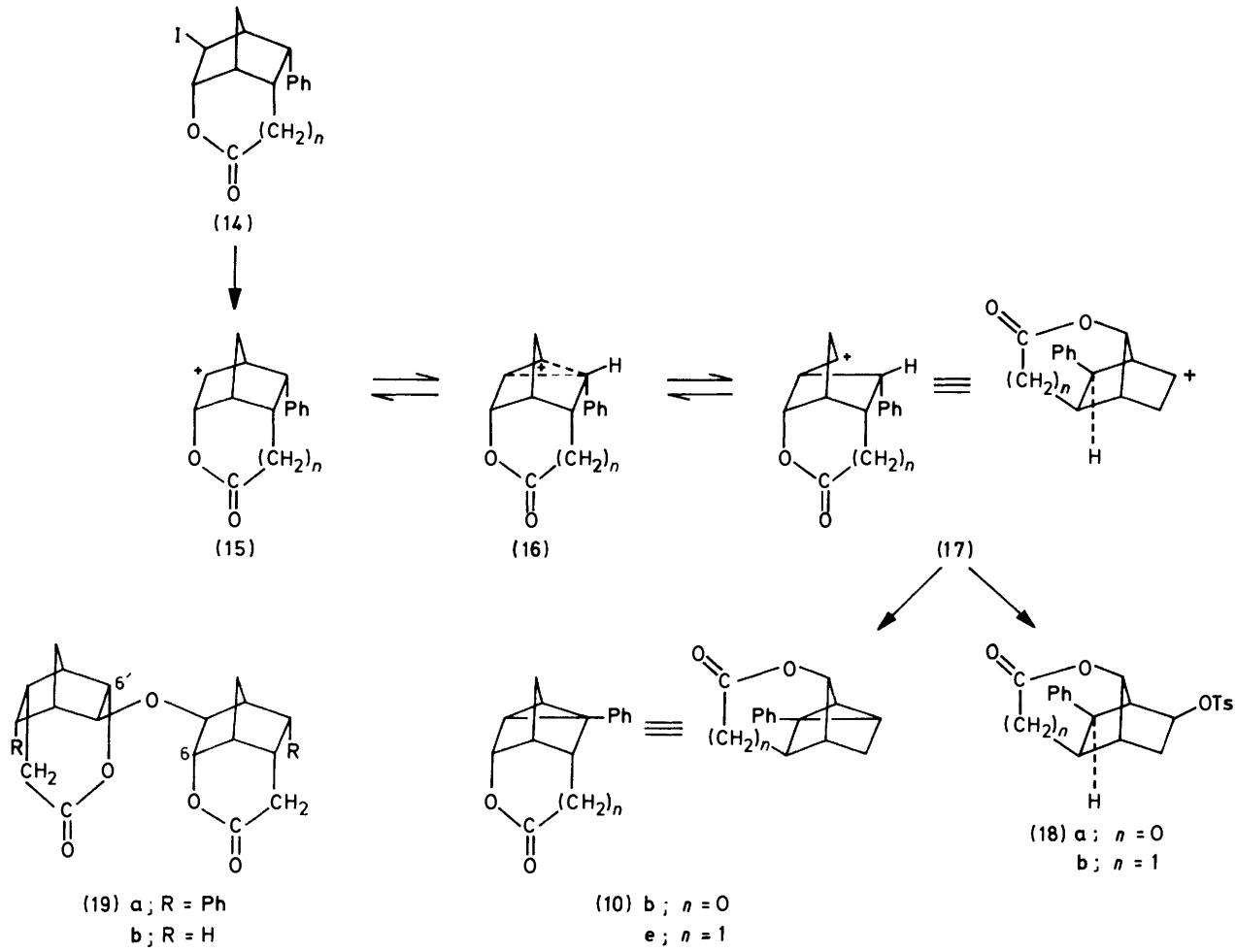


Scheme 1.

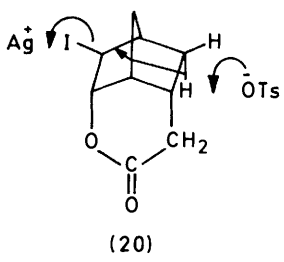
(1d). The ether (19a) is analogous to the ether (19b) which is formed, alongside the nortricyclene lactone (10d) in the reaction of the unsubstituted iodo-δ-lactone (1d) with silver perchlorate.[7] The mechanism for the formation of (19a) is not obvious. Ethers can be formed in the reaction of alkyl iodides with silver oxide,[8] and if silver oxide is produced in the reaction or the silver toluene-4-sulphonate is contaminated with it, then (19a) may have its origin in the reaction of silver oxide with the iodo-δ-lactone (14b) or norbornyl cation (15b).

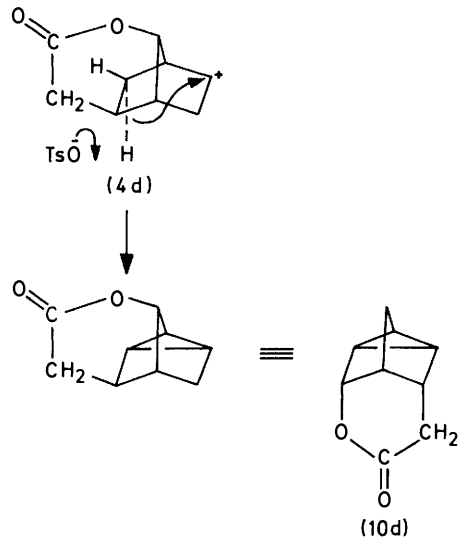
In the case of the 3-*exo*-methyl-iodo-δ-lactone (1f) the initial norbornyl-type cation (2f) may be captured by the toluene-4-sulphonate anion to yield (6f) or undergo rearrangement to cation (4f) from which (7f) is derived. However (2f) undergoes an additional reaction route involving the allowed [9] 3,5-*endo*,*endo*-hydride shift giving the tertiary cation (5f) from which the unsaturated lactone (9) results on proton loss. There appears to be no tendency for (5f) to be captured by a toluene-4-sulphonate anion to afford a tertiary toluene-4-sulphonate as product presumably because of the steric crowding involved. This may be contrasted with the solvolysis [5] of the 6-methylnorborn-2-*exo*-yl toluene-4-sulphonates (21) which give rise to the tertiary cation (22) analogous to (5f). However this cation (22) is less sterically crowded than (5f) and undergoes capture by water to afford the tertiary alcohol (23) and does not undergo proton loss. The steric factors affecting proton loss relative to capture by water are finely balanced and for the 6-isopropylnorborn-2-*exo*-yl toluene-4-sulphonates (24) the more hindered tertiary cation undergoes proton loss to give alkene (26) to a degree comparable with capture by water to afford the tertiary alcohol analogue of (23).

The new results given in this paper, together with those



Scheme 2.

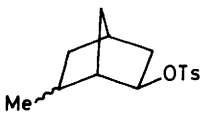




Scheme 3.

reported [2,3,7] earlier, are summarised in the Table and in the mechanistic Schemes 1—3. Norbornyl-type cations (2) are when R = H very prone to give products resulting from Wagner–Meerwein rearrangement of (2) to (4). In the presence of methyl and phenyl substituents the rearrangements (2) ⟶ (4) and (15) ⟶ (17) occur less readily because substituents diminish the stability of the non-classical ion transition states (3) and (16). Such ions would appear to be best thought of as transition states, rather than intermediates, in the interconversion of the classical ions (2) ⟶ (4) and (15) ⟶ (17). However in accordance with the views of Grob [6] these classical ions will almost certainly involve partial bridging between C-3 and C-5 [for (2) and (15)] and between C-4 and C-3 [for (4) and (17)] but this would be well short of that in the fully non-classical ions (3) and (16).

The iodo-γ-lactones (1b),[10] (1c),[11] and (14a) [11] were prepared by literature procedures. The iodo-δ-lactones (1e), (1f), and (14b) were prepared by the respective iodolactonisations of 3-*exo*-phenyl-, 3-*exo*-methyl-, and 3-*endo*-phenyl-norborn-5-en-2-ylacetic acids. 3-Methylnorborn-5-en-2-ylacetic acid



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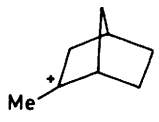

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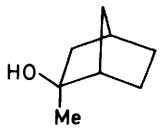

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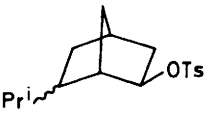

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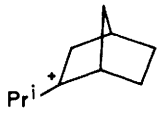

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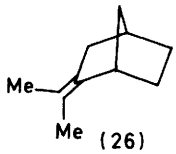

(26)

could be prepared by the hydrolysis of the Diels–Alder adduct of cyclopentadiene and methyl pent-3-enoate. It did not prove possible to prepare 3-*exo*- and 3-*endo*-phenylnorborn-5-en-2-ylacetic acids *via* analogous Diels–Alder reactions. Instead they were prepared by chain extension of their lower homologues 3-*exo*- and 3-*endo*-phenylnorborn-5-ene-2-carboxylic acids in a manner similar to that [12] employed for the chain extension of norborn-5-en-2-ylacetic acid.

Experimental

6-*endo*-Hydroxy-5-*exo*-iodo-3-*exo*-phenylnorborn- (1b), m.p. 124—126.5 °C (lit.,[10] 126—126.5 °C), 6-*endo*-hydroxy-5-*exo*-iodo-3-*exo*-methylnorborn- (1c), m.p. 52—54 °C (lit.,[11] 54—55 °C), and 6-*endo*-hydroxy-5-*exo*-iodo-3-*endo*-phenylnorborn-2-*endo*-ylcarboxylic acid γ-lactone (14a), m.p. 122—123 °C (lit.,[11] m.p. 124 °C), were prepared by literature procedures.

6-endo-*Hydroxy*-5-exo-*iodo*-3-exo-*phenylnorborn*-2-endo-*ylacetic Acid* δ-*Lactone* (1e).—A solution of 3-phenylnorborn-5-ene-2-carboxylic acid (a mixture of the two *trans*-isomers) (7.0 g, 0.03 mol) [11] in anhydrous ether (22 ml) was added slowly over 1 h to a stirred suspension of lithium aluminium hydride (2.0 g, 0.05 mol) in ether (400 ml). The reaction was stirred for a further 1 h after the addition was completed and a saturated solution of ammonium chloride added until a granular precipitate formed. The precipitate was removed by filtration, the filtrate dried ($MgSO_4$), filtered, and the solvent evaporated to give 3-*phenylnorborn*-5-*en*-2-*ylmethanol* (5.3 g, 0.03 mol) as a yellow oil, $\nu_{max.}$ ($CHCl_3$) 3 400 (m, OH) and 1 600 cm^{-1} (m, aromatic); δ(60 MHz, $CDCl_3$) 7.15 (m, Ph), 6.15 (m, 5-, 6-H), 3.50 (dq, 8-H), 2.90 (m, 1-, 4-, 9-H), 2.10 (m, 2-, 3-H), 1.60 (m, 7-*anti*-, 7-*syn*-H); *J* (8a, 8b) 10 Hz; *m/e* 200 (M^+), 182 ($M^+ - H_2O$), 168 ($M^+ - CH_3OH$), and 123 (M^+ — Ph).

A solution of the above alcohol (5.0 g, 0.025 mol) in pyridine (60 ml) was cooled and stirred in an ice–salt bath. Toluene-4-sulphonyl chloride (7.6 g, 0.04 mol) was added slowly and the resultant yellow solution kept in a refrigerator for 40 h during which time crystals of pyridinium hydrochloride gradually formed. The mixture was poured into ice–water (150 g), and the aqueous suspension resulting extracted with ether (4 × 30 ml). The combined ether extracts were washed with 50% (v/v) solution of hydrochloric acid (2 × 50 ml), water (2 × 50 ml), dried ($MgSO_4$), and the solvent evaporated to afford 3-*phenylnorborn*-5-*en*-2-*ylmethyl toluene*-4-*sulphonate* (6.9 g, 0.02 mol) as an oil, $\nu_{max.}$ ($CHCl_3$) 1 600 cm^{-1} (m, aromatic); δ(60 MHz; $CDCl_3$) 7.75 (d, aromatic), 7.25 (d, aromatic), 7.18br (s, Ph), 6.10 (m, 5-, 6-H), 4.0 (dq, 8-H), 2.90br (d, 1-, 4-H), 2.35 (s, Me), 2.40br (s, 3-H), 2.0 (m, 2-H), and 1.52 (m, 7-*anti*-, 7-*syn*-H); *J* (*ortho*-ArH, *meta*-ArH) 8, (8a, 8b) 12 Hz; *m/e* 354 (M^+), 339 (M^+ — Me), 277 and (M^+ — Ph).

Potassium cyanide (2.0 g, 0.03 mol) was added to a solution of this toluene-4-sulphonate (6.7 g, 0.019 mol) in dimethyl sulphoxide (40 ml). The mixture was stirred and heated at 100 °C for 16 h, cooled to room temperature, and then poured into brine (250 ml). The mixture resulting was extracted with chloroform (4 × 50 ml), the combined extracts washed with brine solution (2 × 50 ml) and water (50 ml), dried ($MgSO_4$), filtered, and the solvent evaporated to give 3-*phenylnorborn*-5-*en*-2-*ylmethyl cyanide* (3.33 g, 0.02 mol) as a yellow oil, $\nu_{max.}$ ($CHCl_3$) 2 250 (m, CN) and 1 600 cm^{-1} (m, aromatic); δ(60 MHz; $CDCl_3$) 7.20 (m, Ph), 6.25 (m, 5-, 6-H), 3.0br (s, 4-H), 2.75br (s, 1-H), 2.25 (m, 2-, 8-H), and 1.70 (m, 7-*anti*-, 7-*syn*-H); *m/e* 209 (M^+), 182 (M^+ — HCN), 168 ($M^+ - CH_3CN$), and 132 (M^+ — Ph).

A solution of the cyanide (3.2 g, 0.015 mol) in aqueous potassium hydroxide [KOH (10 g) in water (100 ml)] was stirred and heated at 100 °C for 60 h, cooled, and diluted with water (50 ml). The resulting alkaline solution was extracted with ether (4 × 50 ml), acidified to pH 3 and extracted again with chloroform (5 × 50 ml). The combined chloroform extracts were washed with water (4 × 25 ml), dried ($MgSO_4$), filtered, and evaporated to afford a residue which was distilled to afford 3-*phenylnorborn*-5-*en*-2-*ylacetic acid* (2.80 g, 0.012 mol) as an oil, b.p. 140 °C at 0.2 mmHg (Found: C, 78.9; H, 7.0. $C_{15}H_{16}O_2$ requires C, 78.95; H, 7.0%), $\nu_{max.}$ ($CHCl_3$) 3 500—2 400 (m, CO_2H), 1 710 (s, CO), and 1 600 cm^{-1} (m, aromatic); δ(60 MHz; $CDCl_3$) 11.50 (s, 9-H), 7.20 (m, Ph), 6.20 (m, 5-, 6-H), 2.98br (s, 4-H), 2.80 (m, 3-H, 2.60 (m, 1-H), 2.35 (dq, 8-H), 2.10 (m, 2-H), and 1.65 (m, 7-*anti*-, 7-*syn*-H); *J* (8a, 8b) 12 Hz; *m/e* 228 (M^+), 151 (M^+ — Ph), and 160 ($M^+ - CH_3CO_2H$).

A solution of this acid (2.0 g, 9.77 mmol) in aqueous 0.5N-sodium hydrogencarbonate solution (53 ml) and a solution of iodine (2.25 g, 8.86 mmol) and potassium iodide (8.75 g, 52.72 mmol) in water (28 ml) were mixed and allowed to react according to the method of van Tamelen and Shamma [13] to give 6-endo-*hydroxy*-5-exo-*iodo*-3-exo-*phenylnorborn*-2-endo-*ylacetic acid* δ-*lactone* (1e) (2.20 g, 6.21 mmol) as a crystalline solid, m.p. 108—110 °C [from light petroleum (b.p. 60—80 °C)–ethyl acetate] (Found: C, 50.9; H, 4.5; I, 35.55. $C_{15}H_{15}IO_2$ requires C, 50.85; H, 4.25; I, 35.85%), $\nu_{max.}$ ($CHCl_3$) 1 735 (s, CO) and 1 600 cm^{-1} (m, aromatic); δ(90 MHz; $CDCl_3$) 7.23 (m, Ph), 5.33 (d, 6-*exo*-H), 4.0 (t, 5-*endo*-H), 2.73 (m, 3-*endo*-, 8a-, 8b-H), 2.53br (d, 1-, 2-*exo*-, 4-H), and 2.23 (m, 7-*anti*-, 7-*syn*-H); *J* (1, 6-*exo*) 5, (2-*exo*, 8) 3, (5-*endo*, 6-*exo*) 2, (5-*endo*, 7-*anti*) 2 Hz; *m/e* 354 (M^+), 227 (M^+ — I), and 183 (M^+ — I — CO_2).

6-endo-*Hydroxy*-5-exo-*iodo*-3-exo-*methylnorborn*-2-endo-*ylacetic Acid* δ-*Lactone* (1f).—A mixture of cyclopentadiene (5.03 g, 0.08 mol) and methyl pent-3-enoate [14] (8.70 g, 0.08 mol) was heated in a sealed tube at 180 °C for 200 h. The tube was cooled and opened, ether (150 ml) was added, the insoluble polymeric material removed by filtration, and the ether solution filtrate evaporated to give a viscous yellow oil. The oil was mixed with a 5% (w/w) solution of sodium hydroxide (150 ml) and the mixture heated at reflux for 4 h. The resulting solution was cooled and extracted with ether (3 × 50 ml), acidified to pH 3, and extracted again with ether (5 × 50 ml). The second ether extracts were combined, washed with water (2 × 20 ml), dried ($MgSO_4$), filtered, and the solvent evaporated to afford a brown oil. The oil was distilled to give 3-*methylnorborn*-5-*en*-2-*ylacetic acid* (1.30 g, 8.4 mmol), b.p. 150—152 °C at 0.3 mmHg, $\nu_{max.}$ ($CHCl_3$) 3 200br (CO_2H) and 1 710 cm^{-1} (s, CO); δ(60 MHz; $CDCl_3$) 9.63 (s, 9-H), 6.10 (m, 5-, 6-H), 2.80br (s, 1-H), 2.40br (s,

4-H), 2.20 (m, 8-H), 2.0 (m, 2-H), 1.80 (m, 3-, 7-*anti*-, 7-*syn*-H), and 1.08br (s, 10-H); *m/e* 168 (M^+), 153 (M^+ − Me), and 108 (M^+ − CH_3CO_2H).

A solution of this acid (2.54 g, 0.015 mol) in 0.5N aqueous sodium hydrogencarbonate (110 ml), and a solution of iodine (3.90 g, 0.015 mol) and potassium iodide (15.2 g, 0.09 mol) in water (55 ml) were mixed and allowed to react according to the method of van Tamelen and Shamma [13] to afford 6-endo-*hydroxy*-5-exo-*iodo*-3-exo-*methylnorborn*-2-endo-*ylacetic acid* δ-*lactone* (1f) (2.30 g, 7.8 mmol) as a crystalline solid, m.p. 97—99 °C (from carbon tetrachloride) (Found: C, 41.05; H, 4.45. $C_{10}H_{13}IO_2$ requires C, 41.1; H, 4.45%), $\nu_{max.}$ ($CHCl_3$) 1 730 cm^{-1} (s, CO); δ(90 MHz; C_6D_6) 4.97br (t, 6-*exo*-H), 3.54 (q, 5-*endo*-H), 2.12 (dq, 8a-, 8b-H), 1.71 (m, 1-, 2-*exo*-, 4-H), 1.27 (m, 7-*syn*-H), 1.13 (m, 7-*anti*-H), 0.79 (m, 3-*endo*-H), 0.52 (d, 9-H); *J* (1, 6-*exo*) 4, (2-*exo*, 8a) 3, (2-*exo*, 8b) 5, (3-*endo*, 9) 6, (5-*endo*, 6-*exo*) 2, (5-*endo*, 7-*anti*) 3.2, (8a, 8b) 18 Hz; *m/e* 292 (M^+), 277 (M^+ − Me), 264 (M^+ − CO), and 165 (M^+ − I).

6-endo-*Hydroxy*-5-exo-*iodo*-3-endo-*phenylnorborn*-2-endo-*ylacetic Acid* δ-*Lactone* (14b).—Using the procedures involved in the synthesis of (1e) 3-*endo*-phenylnorborn-5-ene-2-*endo*-ylcarboxylic acid (14a) [11] (6.28 g, 0.029 mol) gave 3-endo-*phenylnorborn*-5-*en*-2-endo-*ylmethanol* (4.04 g, 0.02 mol) as an oil, $\nu_{max.}$ (film) 3 350 (s, OH) and 1 600 cm^{-1} (m, aromatic); δ(60 MHz; $CDCl_3$) 1.55br (s, 7-*anti*-, 7-*syn*-H), 3.00—3.70 (overlapping bands, 1-, 2-, 3-, 4-, 8-H), 6.4 (m, 5-, 6-H), and 7.2 (s, Ph); *m/e* 200 (M^+), 182 (M^+ − H_2O), 168 (M^+ − CH_3OH), and 123 (M^+ − Ph).

This alcohol (4.04 g, 0.02 mol) was converted into 3-endo-*phenylnorborn*-5-*en*-2-endo-*ylmethyl toluene*-4-*sulphonate* (7.03 g, 0.02 mol) as a yellow oil, $\nu_{max.}$ ($CHCl_3$) 1 600 cm^{-1} (m, aromatic); δ(60 MHz; $CDCl_3$) 1.5br (s, 7-*anti*-, 7-*syn*-H), 2.4 (2, Me of OTs), 3.02br (s, 1-, 2-, 4-H), 3.45br (d, 8-H), 3.60br (d, 3-H), 6.00 (m, 6-H), 6.45 (m, 5-H), 7.12br (s, Ph), 7.30 (d, *meta* protons of OTs), and 7.65 (d, *ortho* protons of OTs); *m/e* 354 (M^+), 288, and 155 (Ts^+).

This toluene-4-sulphonate (8.97 g, 0.0253 mol) gave 3-endo-*phenylnorborn*-5-*en*-2-endo-*ylmethyl cyanide* (5.0 g, 0.024 mol) as a brown oil, $\nu_{max.}$ ($CHCl_3$) 2 250 (m, CN) and 1 600 cm^{-1} (m, aromatic); δ(60 MHz; $CDCl_3$) 1.7 (m, 7-*anti*-, 7-*syn*-H), 3.00—3.60 (overlapping bands, 1-, 2-, 3-, 4-, 8-H), 6.20—6.70 (m, 5-, 6-H), and 7.2br (s, Ph); *m/e* 209 (M^+), 182 (M^+ − HCN), 168 (M^+ − CH_3CN), and 132 (M^+ − Ph).

This cyanide (5.0 g, 0.024 mol) afforded 3-endo-*phenylnorborn*-5-*en*-2-endo-*ylacetic acid* (1.5 g, 6.6 mmol) as an oil, $\nu_{max.}$ (CH_2Cl_2) 2 500—3 500br (CO_2H), 1 700 (s, CO), and 1 600 cm^{-1} (m, aromatic); δ(60 MHz; $CDCl_3$) 1.6br (s, 7-*anti*-, 7-*syn*-H), 1.80—1.90 (m, 1-, 2-, 4-H), 3.05 (m, 8a-, 8b-H), 3.5br (d, 3-H), 6.20—6.60 (m, 5-, 6-H), and 7.15br (s, Ph); *m/e* 228 (M^+) and 168 (M^+ − CH_3CO_2H).

This acid (1.5 g, 6.6 mmol) using the method of van Tamelen and Shamma [13] afforded 6-endo-*hydroxy*-5-exo-*iodo*-3-endo-*phenylnorborn*-2-endo-*ylacetic acid* δ-*lactone* (14b) (0.7 g, 2.0 mmol) as a crystalline solid, m.p. 144—145 °C [from 7 : 7 : 6 light petroleum (b.p. 60—80 °C)–ethyl acetate–carbon tetrachloride] (Found: C, 50.8; H, 4.4; I, 35.8. $C_{15}H_{15}IO_2$ requires C, 50.85; H, 4.3; I, 35.85%), $\nu_{max.}$ (CH_2Cl_2) 1 730 (s, CO) and 1 600 cm^{-1} (m, aromatic); δ(250 MHz; $CDCl_3$) 1.94 (d of pentets, 7-*anti*-H), 2.34br (d, 7-*syn*-H), 2.60 (dd, 8b-H), 2.72 (dd, 8a-H), 2.62br (s, 1-H underneath 8b-H), 2.88 (m, 2-H), 3.02br (s, 4-H), 3.62 (dd, 3-*exo*-H), 4.26 (t, 5-*endo*-H), 5.22 (pentet, 6-*exo*-H), 7.05br (d, *ortho* protons of Ph), and 7.25—7.43 (m, *meta* and *para* protons of Ph); *J* (2-*exo*, 3-*exo*) 11.5, (2-*exo*, 8a) 8.0 (2-*exo*, 8b) 2.0, (3-*exo*, 4) 3.5, (5-*endo*, 6-*exo*) 3.3, (5-*endo*, 7b) 3.3, (7-*anti*, 7-*syn*) 11.0, (8a, 8b) 19.5 Hz; *m/e* 227 (M^+ − I), 209 (227 − H_2O), and 171 (227 − CO_2 − H_2O).

General Method for the Reaction of Iodolactones with Silver Toluene-4-sulphonate.—A solution of iodolactone (10 mmol) in anhydrous acetonitrile (20 ml) was added dropwise over 1 h to a well stirred solution of silver toluene-4-sulphonate [15] (22.5 mmol) in anhydrous acetonitrile (40 ml) cooled in an ice-bath to 5 °C and protected from light under nitrogen. After the addition was completed the stirred solution was kept at 5 °C for a further 1 h and then allowed to reach room temperature over the next hour. The mixture was then heated at a particular temperature for a stated time as a yellow precipitate of silver iodide gradually formed. The acetonitrile solution was decanted, the silver iodide precipitate washed with water (40 ml), and the washings added to the acetonitrile solution. The resultant solution was extracted with dichloromethane (4 × 40 ml) and the extracts combined and filtered through Celite. The filtrate was washed with water (2 × 60 ml), dried ($MgSO_4$), filtered, and the solvent evaporated to afford the product.

Reaction of 6-endo-*Hydroxy*-5-exo-*iodo*-3-exo-*methylnorborn*-2-endo-*ylcarboxylic Acid* γ-*Lactone* (1c) *with Silver Toluene*-4-*Sulphonate.*—A solution of the γ-iodolactone (1c) (1.02 g, 4 mmol) in anhydrous acetonitrile (12 ml) was added to a solution of silver toluene-4-sulphonate (4.0 g, 14.3 mmol) in anhydrous acetonitrile (30 ml). The mixture was then heated at reflux for 40 h and worked-up to afford a semi-solid product which was separated by preparative layer chromatography [2 : 3 ethyl acetate–light petroleum (b.p. 60—80 °C), 60 × 20 × 0.1 cm silica gel plates] into the following components:

(i) the unchanged γ-iodolactone (1c) (0.18 g, 0.71 mmol), R_F 0.75 as crystals, m.p. 52—54 °C;

(ii) 6-endo-*hydroxy*-3-exo-*methyl*-5-exo-p-*tolysulphonyloxynorborn*-2-endo-*ylcarboxylic acid* γ-*lactone* (6c) (0.27 g, 0.83 mmol), R_F 0.52, as a crystalline solid, m.p. 77—78 °C (from pentane–ether) (Found: C, 59.65; H, 5.65; S, 9.85. $C_{16}H_{18}O_5S$ requires C, 59.65; H, 5.6; S, 9.95%), $\nu_{max.}$ ($CHCl_3$) 1 790 (s, CO) and 1 600 cm^{-1} (m, aromatic); δ(90 MHz; $CDCl_3$) 7.75 (d, ArH), 7.35 (d, ArH), 4.45br (d, 6-*exo*-H), 4.22br (s, 5-*endo*-H), 3.13br (t, 1-H), 2.46 (s, Me), 2.13br (s, 4-H), 2.06br (d, 2-*exo*-H), 1.89 (m, 7-*anti*-, 7-*syn*-H), 1.78 (m, 3-*endo*-H), and 1.09 (d, Me); *J* (1, 2-*exo*) 6, (1, 6-*exo*) 6, (3-*endo*, Me) 8, (*ortho*-ArH, *meta*-ArH) 8 Hz; *m/e* 322 (M^+), 307 (M^+ − Me), and 151 (M^+ − $C_7H_7SO_2$);

(iii) 7-syn-*hydroxy*-5-endo-*methyl*-3-exo-p-*tolylsulphonyloxynorborn*-6-exo-*ylcarboxylic acid* γ-*lactone* (7c) (0.11 g, 0.34 mmol), R_F 0.43, as a crystalline solid, m.p. 115—117 °C (from pentane–ether) (Found: C, 59.65; H, 5.75; S, 9.65%), $\nu_{max.}$ ($CHCl_3$) 1 780 (s, CO) and 1 600 cm^{-1} (m, aromatic); δ(90 MHz; $CDCl_3$) 7.75 (d, Ar-H), 7.35 (d, ArH), 5.03br (s, 7-*anti*-H), 4.85br (q, 3-*endo*-H), 2.69 (m, 6-*endo*-H), 2.54br (d, 1-H), 2.46 (s, Me), 2.28 (m, 4-H), 2.23 (m, 2-*exo*-H), 2.03 (q, 2-*endo*-H), 1.90br (d, 5-*exo*-H), and 1.07 (d, Me); *J* (1, 2-*exo*) 6, (2-*endo*, 3-*endo*) 6, (4, 5-*exo*) 5, (5-*exo*, Me) 7 Hz; *m/e* 322 (M^+), 307 (M^+ − Me), and 314 (M^+ − CO).

Reaction of 6-endo-*Hydroxy*-5-exo-*iodo*-3-exo-*phenylnorborn*-2-endo-*ylacetic Acid* δ-*Lactone* (1e) *with Silver Toluene*-4-*sulphonate.*—A solution of the δ-iodolactone (1e) (0.98 g, 2.8 mmol) in anhydrous acetonitrile (10 ml) was added dropwise over 45 min to a well stirred solution of silver toluene-4-sulphonate (2.3 g, 6.4 mmol) in anhydrous acetonitrile (20 ml) cooled in an ice-bath to 5 °C and protected from light under nitrogen. After the addition was completed, the ice-bath was removed and the temperature allowed to rise to room temper-

ature over the next hour. The mixture was then heated at 55 °C for 16 h and worked up to afford a yellow oil (0.94 g) which was separated by column chromatography [silica gel Merck H Type 60 (50 g) with 2 : 3 ethyl acetate–light petroleum (b.p. 60—80 °C) as eluant] into the following components:

(i) 6-endo-*hydroxy*-3-exo-*phenyl*-5-exo-p-*tolylsulphonyl-oxynorborn*-2-endo-*ylacetic acid* δ-*lactone* (6e) (0.40 g, 1 mmol), R_F 0.39, as a crystalline solid, m.p. 188—189 °C (Found: C, 66.05; H, 5.65; S, 7.85. $C_{22}H_{22}O_5S$ requires C, 66.35; H, 5.55; S, 8.05%); $\nu_{max.}$ ($CHCl_3$) 1 734 (s, CO) and 1 598 cm^{-1} (m, aromatic); δ(90 MHz; $CDCl_3$) 7.80 (d, ArH), 7.32 (d, ArH), 7.22 (m, Ph), 4.69 (d, 6-*exo*-H), 4.42br (s, 5-*endo*-H), 2.66br (d, 3-*endo*-, 8a-, 8b-H), 2.57 (m, 4-H), 2.44 (s, Me), 2.36 (m, 1-H), 2.32 (m, 2-*exo*-H), and 1.97 (m, 7-*anti*-, 7-*syn*-H); *J* (1, 6-*exo*) 4, (*ortho*-ArH, *meta*-ArH) 8 Hz; *m/e* 398 (M^+), 226 ($M^+ - C_7H_7OSO_2$), and 165 ($M^+ - C_7H_7SO_2 - Ph$);

(ii) 7-syn-*hydroxy*-5-endo-*phenyl*-3-exo-p-*tolylsulphonyl-oxynorborn*-6-exo-*ylacetic acid* δ-*lactone* (7e) (0.32 g, 0.8 mmol), R_F 0.26, as crystals, m.p. 191—192 °C (Found: C, 66.25; H, 5.7; S, 7.85%), $\nu_{max.}$ ($CHCl_3$) 1 738 cm^{-1} (s, CO); δ(90 MHz; $CDCl_3$) 7.46 (d, ArH), 7.30 (d, ArH), 7.11 (m, Ph), 4.92br (d, 7-*anti*-H), 4.02 (t, 3-*endo*-H), 3.15 (d, 5-*exo*-H), 2.77 (d, 4-H), 2.66br (d, 8a-, 8b-H), 2.49 (d, 6-*endo*-H), 2.43 (s, Me), 2.29br (s, 1-H), and 1.89 (m, 2-*exo*-, 2-*endo*-H); *J* (2-*exo*, 3-*endo*) 5, (2-*endo*, 3-*endo*) 5, (4,5-*exo*) 5, (6-*endo*, 7-*syn*) 2, (*ortho*-ArH, *meta*-ArH) 8 Hz; *m/e* 398 (M^+) and 217 ($M^+ - C_7H_7SO_2OH$);

(iii) 7-anti-*hydroxy*-5-endo-*phenylnorborn*-2-*en*-6-exo-*ylacetic acid* δ-*lactone* (8e) (60 mg, 0.265 mmol), R_F 0.58, as an oil, b.p. 150 °C at 0.08 mmHg (Found: C, 79.45; H, 6.15. $C_{15}H_{14}O_2$ requires C, 79.05; H, 6.2%), $\nu_{max.}$ ($CHCl_3$) 1 735 cm^{-1} (s, CO); δ(90 MHz; $CDCl_3$) 7.20 (m, Ph), 6.24 (q, 2-H), 5.77 (q, 3-H), 4.33 (d, 7-*syn*-H), 3.25 (m, 4-, 5-*exo*-H), 3.0 (q, 8b-H), 2.78br (s, 1-H), 2.71 (q, 8a-H), and 2.39 (m, 6-*endo*-H); *J* (2, 3) 6, (5-*exo*, 6-*endo*) 4, (6-*endo*, 7-*syn*) 3, (6-*endo*, 8a) 4, (6-*endo*, 8b) 4, (8a, 8b) 17 Hz; *m/e* 226 (M^+), 166 ($M^+ - CH_3CO_2H$), and 160 ($C_{10}H_8O_2^+$).

Reaction of 6-endo-*Hydroxy*-5-exo-*iodo*-3-exo-*methyl-norborn*-2-endo-*ylacetic Acid* δ-*Lactone* (1f) *with Silver Toluene*-4-*sulphonate*.—A solution of the δ-iodolactone (1f) (2.4 g, 8.2 mmol) in anhydrous acetonitrile (20 ml) was added dropwise over 45 min to a well stirred solution of silver toluene-4-sulphonate (6.3 g, 23 mmol) in anhydrous acetonitrile (35 ml) cooled in an ice-bath to 5 °C and protected from light under nitrogen. After addition was complete, the ice-bath was removed and the temperature allowed to rise to room temperature over the next hour. The mixture was then stirred at room temperature for 16 h and worked up to afford a yellow oil (1.5 g) which was separated by preparative layer chromatography [2 : 3 ethyl acetate–light petroleum (b.p. 60—80 °C); 60 × 20 × 0.1 cm silica gel plates] into the following components:

(i) 6-endo-*hydroxy*-3-*methylenenorborn*-2-endo-*ylacetic acid* δ-*lactone* (9f) (0.48 g, 2.93 mmol), R_F 0.47, as a pale yellow oil, (Found: C, 72.95; H, 7.3. $C_{10}H_{12}O_2$ requires C, 73.15; H, 7.3%); $\nu_{max.}$ ($CHCl_3$) 1 735 cm^{-1} (s, CO); δ(90 MHz; $CDCl_3$) 5.05 (d, 9a-H), 4.94 (m, 6-*exo*-H), 4.82 (d, 9b-H), 2.75 (m, 1-, 4-, 8a-, 8b-H), 2.54 (m, 2-*exo*-H), 2.22 (dq, 5-*exo*-H), 1.57 (m, 7-*anti*-, 7-*syn*-H), 1.40 (dt, 5-*endo*-H); *J* (4, 5-*exo*), (5-*exo*, 5-*endo*) 14, (5-*exo*, 6-*exo*) 10, (5-*endo*, 7-*anti*) 3, (9a, 9b) 2 Hz; *m/e* 164 (M^+), 136 ($M^+ - CO$), 122 ($M^+ - C_2H_2O$), and 92 ($M^+ - C_3H_3O_2$);

(ii) 6-endo-*hydroxy*-3-exo-*methyl*-5-exo-p-*tolylsulphonyl-oxynorborn*-2-endo-*ylacetic acid* δ-*lactone* (6f) (0.42 g, 1.25 mmol), R_F 0.27, as a crystalline solid, m.p. 132—134 °C [ethyl acetate–light petroleum (b.p. 60—80 °C)] (Found: C, 60.65; H, 6.0; S, 9.3. $C_{17}H_{20}O_5S$ requires C, 60.7; H, 5.95; S, 9.3%), $\nu_{max.}$ ($CHCl_3$) 1 735 cm^{-1} (s, CO); δ(90 MHz; $CDCl_3$) 7.75 (d, ArH), 7.35 (d, ArH), 4.80 (q, 6-*exo*-H), 4.72 (d, 5-*endo*-H), 2.57 (d, 8a-, 8b-H), 2.46 (s, Me), 2.42br (s, 4-H), 2.13 (m, 1-H), 1.90 (m, 7-*anti*-, 7-*syn*-H), 1.82 (d, 3-*endo*-H), 1.53 (m, 2-*exo*-H), and 1.0 (d, Me); *J* (1, 6-*exo*), 6, (2-*exo*, 8) 3, (3-*endo*, Me) 8, (5-*endo*, 7-*anti*) 3, (*ortho*-ArH, *meta*-ArH) 8 Hz; *m/e* 336 (M^+), 321 ($M^+ - Me$), and 164 ($M^+ - C_7H_7SO_3$);

(iii) 7-syn-*hydroxy*-5-endo-*methyl*-3-exo-p-*tolylsulphonyl-oxynorborn*-6-exo-*ylacetic acid* δ-*lactone* (7f) (0.3 g, 0.89 mmol), R_F 0.33, as a crystalline solid, m.p. 140—141 °C [ethyl acetate–light petroleum (b.p. 60—80 °C)] (Found: C, 60.4; H, 5.75; S, 9.2%), $\nu_{max.}$ ($CHCl_3$) 1 735 cm^{-1} (s, CO); δ(90 MHz; $CDCl_3$) 7.80 (d, ArH), 7.33 (d, ArH), 4.58 (d, 3-*endo*-H), 4.27br (s, 7-*anti*-H), 2.54 (d, 8a-, 8b-H), 2.44 (s, Me), 2.42br (s, 4-H), 2.10 (m, 1-H), 1.70 (m, 2-*exo*-, 5-*exo*-, 6-*endo*-H), and 1.0 (d, Me); *J* (5-*exo*, Me) 6, (6-*endo*, 8) 3, (*ortho*-ArH, *meta*-ArH) 8 Hz; *m/e* 366 (M^+) and 351 ($M^+ - Me$).

Reaction of 6-endo-*Hydroxy*-5-exo-*iodo*-3-endo-*phenylnorborn*-2-endo-*ylcarboxylic Acid* γ-*Lactone* (14a) *with Silver Toluene*-4-*sulphonate*.—A solution of the γ-iodolactone (14a) (1.0 g, 2.9 mmol) in anhydrous acetonitrile (6 ml) was added dropwise during 1 h to a well stirred solution of silver toluene-4-sulphonate (1.5 g, 5.4 mmol) in anhydrous acetonitrile (30 ml) cooled in an ice–water-bath. The reaction was performed under nitrogen and with protection from moisture and light. After completion of the addition, the ice-bath was removed and the mixture was warmed to room temperature over the next 25 min. The mixture was then heated at reflux for 42 h and worked up to afford a thick black oil (0.54 g) which was separated by preparative layer chromatography [3 : 7 ethyl acetate–light petroleum (b.p. 60—80 °C); 60 × 20 × 0.1 cm silica gel plates] into the following components:

(i) 6-endo-*hydroxy*-3-*phenylnortricycl*-2-endo-*ylcarboxylic acid* γ-*lactone* (10b) (0.23 g, 1.08 mol), R_F 0.4, as a crystalline solid, m.p. 91.0—91.5 °C [from 1 : 4 ethyl acetate–light petroleum (b.p. 60—80 °C)] (Found: C, 78.8; H, 5.75. $C_{14}H_{14}O_2$ requires C, 79.2; H, 5.7%), $\nu_{max.}$ (CH_2Cl_2) 1 770 (s, CO), and 1 600 cm^{-1} (m, aromatic); δ(250 MHz; $CDCl_3$) 1.97br (t, 7-*anti*-, 7-*syn*-H), 2.12 (dd, 5-H), 2.29 (dm, 4-H), 2.76br (s, 1-H), 3.09 (d, 2-H), 4.91 (t, 6-H), 7.30 (m, aromatic); *J* (1, 2) 2.2, (1, 6) 2.5, (4, 5) 5, (5, 6) 2.5 Hz; *m/e* 212 (M^+), 184 ($M^+ - CO$), 168 ($M^+ - CO_2$), 155 ($M^+ - CHCO_2$), and 77 (Ph^+);

(ii) 7-syn-*hydroxy*-5-exo-*phenyl*-3-exo-p-*tolylsulphonyl-oxynorborn*-6-exo-*ylcarboxylic acid* γ-*lactone* (18a) (0.228 g, 0.59 mmol), R_F 0.16, as a crystalline solid, m.p. 135—136 °C (Found: C, 65.1; H, 5.2. $C_{21}H_{20}O_5S$ requires C, 65.6; H, 5.25%), $\nu_{max.}$ (CH_2Cl_2) 1 795 (s, CO) and 1 600 cm^{-1} (m, aromatic); δ(250 MHz; $CDCl_3$) 1.96br (dd, 2-*exo*-H), 2.20 (dd, 2-*endo*-H), 2.46 (s, Me), 2.92 (m, 1-, 4-, 6-H), 4.80 (d, 3-*endo*-H), 5.14br (s, 7-*anti*-H), 7.12br (d, *meta*-protons of OTs), 7.30 (m, Ph), and 7.80 (d, *ortho*-protons of OTs); *J* (1, 2-*exo*) 5, (2-*exo*, 2-*endo*) 16, (2-*endo*, 3-*endo*) 7 Hz; *m/e* 384 (M^+), 229 ($M^+ - TsOH$), 184 (212 − CO), and 168 (212 − CO_2).

Reaction of 6-endo-*Hydroxy*-5-exo-*iodo*-3-endo-*phenylnorborn*-2-endo-*ylacetic Acid* δ-*Lactone* (14b) *with Silver Toluene*-4-*sulphonate*.—A solution of the δ-lactone (14b) (0.2 g, 0.57 mmol) in anhydrous acetonitrile (4 ml) was added dropwise to a well stirred solution of silver toluene-4-sulphonate (0.3 g, 1.1 mmol) in anhydrous acetonitrile (10 ml) cooled in an ice–water-bath. The reaction was performed under nitrogen and with protection from light. After the addition of the iodolactone was completed, the ice–water-bath was removed and

the temperature of the reaction mixture was allowed to reach room temperature. The mixture was then heated at reflux for 48 h to give a dark oil (0.105 g) which was separated by preparative layer chromatography ($CHCl_3$; 20 × 20 × 0.1 cm silica gel plate) into the following components:

(i) 6-endo-*hydroxy*-3-*phenylnortricycl*-2-endo-*ylacetic acid* δ-*lactone* (10e) (30 mg, 0.133 mmol), R_F 0.6, as an oil, $\nu_{max.}$ (CH_2Cl_2) 1 730 (s, CO) and 1 600 cm^{-1} (m, aromatic); δ(250 MHz; $CDCl_3$) 1.66 (dm, 4-H), 1.75br (d, 7-*syn*-H), 1.81 (dt, 7-*anti*-H), 2.14 (dm, 5-H), 2.26br (s, 1-H), 2.57br (s, 2-H), 2.68 (dd, 8b-H), 2.77 (dd, 8a-H), 4.68br (s, 6-H), and 7.10—7.40 (m, aromatic-H); *J* (1, 7-*anti*) 1.5, (1, 7-*syn*) 1.5, (2, 8a) 2, (2, 8b) 4, (4, 5) 6, (4, 7-*anti*) 1.5, (5, 6) 1.5, (7-*syn*, 7-*anti*) 11.5, (8a, 8b) 18.5 Hz; *m/e* 226 (M^+), 155 ($M^+ - CHCH_2CO_2$), 141 ($M^+ - CH_2CHCH_2CO_2$), and 128 ($M^+ - CHCH_2CHCH_2CO_2$);

(ii) the ether (19a) (25 mg, 0.053 mmol), R_F 0.46, as an oil, $\nu_{max.}$ (CH_2Cl_2) 1 730 (s, CO) and 1 600 cm^{-1} (m, aromatic); δ(60 MHz; $CDCl_3$) 1.2—1.8 (overlapping resonances integrating for 10 H, 1-, 4-, 7-*anti*-, 7-*syn*-, 1′-, 4′-, 7′-*anti*-, 7′-*syn*-H), 2.6—3.5 (overlapping resonances integrating for 6 H, 3-, 8a-, 8b-, 3′-, 8′a-, 8′b-H), 4.00 (m, 5-*endo*-, 5′-*endo*-H), 5.0 (m, 6-*exo*, 6′-*exo*-H), and 7.4 (m, Ph); *m/e* 470 (M^+), 244 ($C_{15}H_{16}O_3^+$), and 266 ($C_{15}H_{14}O_2^+$).

Product proportions were obtained by comparing the integration of 6-*exo*-H of the tricyclic lactone (10e) and of 6-*exo*-H plus 6-′*exo*-H of the ether (19a) in the n.m.r. spectrum of the crude mixture and found to be 8 : 1.

Product proportions in the reaction of norbornane iodolactones with silver toluene-4-sulphonate

Lactone	Percentage † of product from initially formed cation (2) or (15)	Percentage † of product from Wagner–Meerwein rearranged cation (4) or (17)
(1a) [1]		(7a) 100
(1b) [2]	(6b) 19.7, (11) 71.2	(7b) 9.1
(1c)	(6c) 71	(7c) 29
(1d) [7]		(7d) 43.7, (10d) 56.3
(1e)	(6e) 51.3	(7e) 41.0, (8e) 7.7
(1f)	(6f) 24.7, (9) 57.9	(7f) 17.6
(14a)		(10b) 64.7, (18a) 35.3
(14b)	(19a) 11.1	(10e) 88.9

† Percentages are based on isolated yields and n.m.r. of product mixtures.

Acknowledgements

The Malaysian Government (A. S. and S. N.) and the Association of Commonwealth Universities (S. N.) are thanked for the award of research studentship.

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Received 29*th July* 1982; *Paper* 2/1311