Product Formation and Identification in the Reaction of 6-*endo*-Hydroxy-5-*exo*-iodo-3-*exo*-phenylnorborn-2-*endo*-ylcarboxylic Acid γ-Lactone with Silver Toluene-*p*-sulphonate

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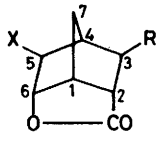
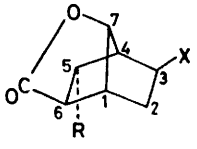
The reaction of 6-*endo*-hydroxy-5-*exo*-iodonorborn-2-*endo*-ylcarboxylic acid γ-lactone with silver toluene-*p*-sulphonate affords 7-*syn*-hydroxy-3-*exo*-tosyloxynorborn-6-*exo*-ylcarboxylic acid γ-lactone as the sole product. A comparable reaction with 6-*endo*-hydroxy-5-*exo*-iodo-3-*exo*-phenylnorborn-2-*endo*-ylcarboxylic acid γ-lactone affords a mixture of 6-*endo*-hydroxy-3-*exo*-phenyl-5-*exo*-tosyloxynorborn-2-*endo*-ylcarboxylic acid γ-lactone, 7-*syn*-hydroxy-5-*endo*-phenyl-3-*exo*-tosyloxynorborn-6-*exo*-ylcarboxylic acid γ-lactone, and 2-*exo*-hydroxy-4-phenylnorborn-5-en-7-*anti*-ylcarboxylic acid γ-lactone. Product formation is discussed in terms of possible carbocation intermediates. The latter product is unusual in that the position of the bridgehead C-1 proton in the ^{1}H n.m.r. spectrum is similar to that of the aromatic protons. Product structures were determined by n.m.r. spectroscopic studies, and by chemical conversions.

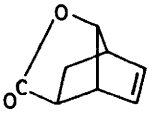
As part of a study of neighbouring group dipolar effects upon solvolytic reactivity, Moriarty *et al.*[1] studied the acetolysis of 5-*exo*-tosyloxy-6-*endo*-hydroxynorborn-2-*endo*-ylcarboxylic acid γ-lactone (1a). The sole product



(1) a; R = H, X = OTs
b; R = H, X = I
c; R = Ph, X = I
d; R = Ph, X = OTs



(2) a; R = H, X = OAc
b; R = H, X = OTs
c; R = Ph, X = OTs



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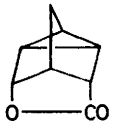

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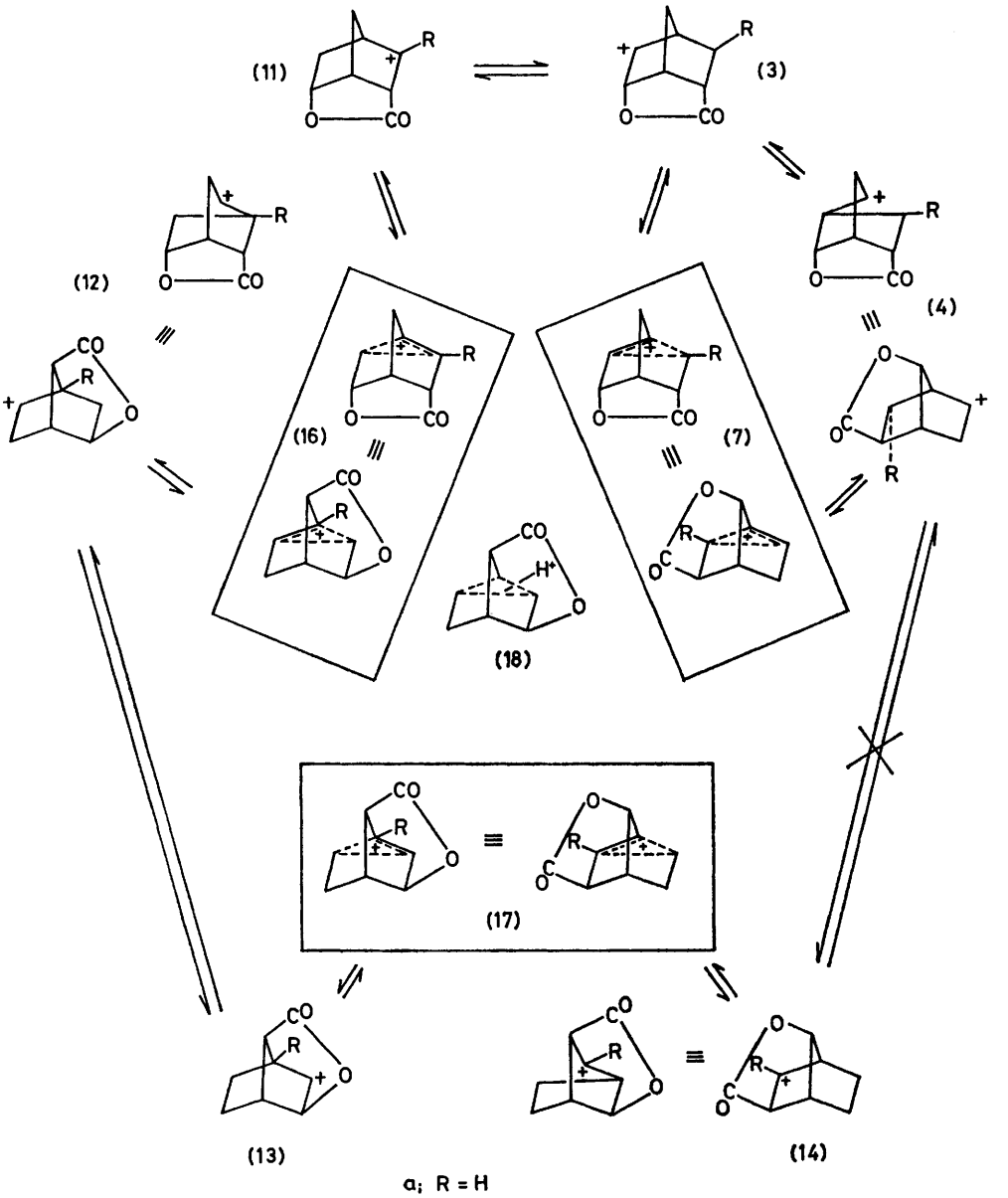
was 3-*exo*-acetoxy-7-*syn*-hydroxynorborn-6-*exo*-ylcarboxylic acid γ-lactone (2a). It was proposed that the intermediate carbocation (3a), underwent a Wagner–Meerwein rearrangement to give cation (4a), which was captured by acetic acid to afford (2a). The photolysis of the iodolactone (1b) was shown by Kropp [2] to afford the unsaturated lactone (5) and the nortricyclene lactone (6) as important products. Although the photochemistry of iodides is not normally recognised [3] as a reaction involving carbocations, Kropp considered the non-classical ion (7a) which is a composite of the classical ions (3a) and (4a), to be involved in product formation. Because of the possible ambiguity in the photochemistry of alkyl iodides as a means of producing carbocations, it was desirable to seek an alternative method of producing such intermediates from the iodolactone (1b). The method chosen was that of Hoffmann,[4] who showed that an alkyl iodide, when treated with silver toluene-*p*-sulphonate in acetonitrile solution, affords an alkyl toluene-*p*-sulphonate *via* an intermediate carbocation. When we applied this method to the iodolactone (1b) the sole product had the rearranged structure (2b). This formation of (2b) will almost certainly involve the same intermediate carbocations [(3a) and (4a)] as participate in the acetolysis of the toluene-*p*-sulphonate (1a) to give the rearranged acetate (2a). Since (2a) and (2b) are derived from carbocations, and are related to the product (5) formed in the photolysis of (1b), it is likely that (2a), (2b), and (5) all have a similar mechanistic origin. This gives support to the view of Kropp,[2] at least in so far as the formation of (5) is concerned, that the photolysis of (1b) involves carbocation intermediates.

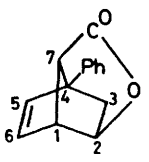
An extension of this method to the reaction of the 3-*exo*-phenyl-substituted iodolactone (1c) provided an unexpected result, since in addition to the toluene-*p*-sulphonate (2c), anticipated on the basis of the results with the unsubstituted iodolactone (1b), the toluene-*p*-sulphonate (1d) and the unsaturated lactone (8) were also formed. These products (2c), (1d), and (8) were isolated in a 1 : 2.2 : 6.4 molar ratio. On the basis of their n.m.r. data (given in the Experimental section) and a knowledge of the n.m.r. of norbornanes [5] and norbornane lactones [6] the product (1d) was readily identified, as was (2c) with the additional help of the spin-decoupling experiments reported in the Table. Ready identification was not achieved with the unsaturated lactone (8), since it had a ^{1}H n.m.r. spectrum which proved difficult to interpret. In the aromatic region a multiplet was observed centred at δ 7.50 integrating for six protons. That the additional non-aromatic proton in this region was *not* an olefinic proton shifted to lower field was clear since the olefinic protons at C-5 and C-6 appeared as a multiplet at δ 5.99 integrating for two protons. Decoupling experiments (Table) identify this exceptionally low-field proton as the bridgehead proton at C-1, which would have been anticipated from n.m.r. spectral studies of norbornenes [7] to be in the region δ 2.5—3.5. The remarkable downfield shift to δ 7.50 must be because

the geometry of the molecule is such that one observes an additive deshielding effect of H-1 due to the anisotropy of the double bond, the aromatic ring, and the ester carbonyl group, as well as the inductive effect of ester oxygen. Reduction of the unsaturated lactone (8) with lithium aluminium hydride afforded the unsaturated diol (9), the n.m.r. spectrum of which showed H-1 had moved to the somewhat higher field of δ 6.65; still a remarkably low-field position but illustrating the anisotropic deshielding effect of the lactone carbonyl group in (8). Oxidation of the unsaturated diol (9) with pyridinium dichromate [8] produced the unsaturated keto-aldehyde (10), the n.m.r. spectrum of which showed H-1 to be at δ 7.65, an even lower-field position than in (8), the most likely cause of which is additional anisotropic deshielding due to the presence of the C-2 carbonyl group. The structural assignments for (9) and (10) are supported by spin-decoupling experiments (Table).

The most satisfactory explanation of these results involves the equilibrating classical ions (3b), (4b), and (11b)—(14b). Ionisation of (1c) affords (3b) which may be captured by toluene-*p*-sulphonate ion to give (1d). Alternatively (3b) may undergo a Wagner–Meerwein rearrangement to afford (4b), from which (2c) is derived. However, (2c) and (1d) are relatively minor products, and the formation of the major product (8) requires an alternative route. This necessitates (3b) undergoing a 3,5-*endo*,*endo* hydride [9] shift to give the more stable



benzyl-type norbornyl cation (11b). This is not captured by toluene-*p*-sulphonate ion to give products, probably for steric reasons, and instead undergoes a Wagner–Meerwein rearrangement to afford (12b), from which (8) is derived by loss of a proton. There appears at



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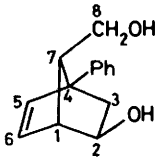

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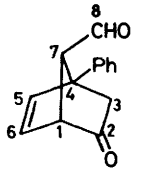


(10)

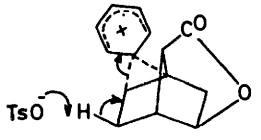
first sight no obvious reason why (12b) should not be captured by a toluene-*p*-sulphonate ion to give a product, and therefore ion (12b) may be additionally stabilised by the involvement of a phenonium-type contributor such as (15), from which proton loss by the toluene-*p*-sulphonate ion acting as a base may be a feasible route to product formation. No products were obtained derived from ions (13b) and (14b), which could potentially

TABLE

Spin-decoupling experiments on compounds (2c), (8), (9), and (10)

Compound	Irradiated protons	δ	Observations
(2c)	H-1, H-4	2.90	Sharpening of br s at δ 5.15 of H-7-*anti*, br q at δ 1.96 of H-2-*endo* becomes a sharp q, *J*(2-*endo*, 2-*exo*) 16 and *J*(2-*endo*, 3-*endo*) 6 Hz, collapse of m at δ 1.65 of H-2-*exo* to a q, *J*(2-*endo*,-2-*exo*) 16 and *J*(2-*exo*, 3-*endo*) 2 Hz.
	H-3-*endo*	4.08	Collapse of q at δ 1.96 of H-2-*endo* to a d, *J*(2-*endo*,2-*exo*) 16 Hz, together with small changes in m at δ 1.65 of H-2-*exo*
	H-5-*exo*	3.41	Changes at δ 2.90 (H-4) and δ 3.18 (H-6-*endo*)
	H-7	5.15	Collapse of t at δ 3.18 of H-6-*endo* to a d, *J*(5-*exo*, 6-*endo*) 2 Hz, together with small changes at δ 2.90 (H-1) and δ 1.96 (H-2-*endo*)
(8)	H-2-*endo*	5.60	Collapse of m at δ 4.0 of H-7-*syn*, dd at δ 3.10 of H-3-*endo*, and dm at δ 2.4 of H-3-*exo*
	H-3-*endo*	3.10	Collapse of dm at δ 2.4 of H-3-*exo* to two overlapping d, *J*(2-*endo*,3-*exo*) 5 and *J*(3-*exo*,5-*exo*) 2 Hz
	H-3-*exo*	2.40	Collapse of dd at δ 3.10 of H-3-*endo* and of m at δ 4.0 of H-7-*syn*, and small changes at δ 5.99 (H-5-*exo*)
	H-1	7.50	Sharpening of m at δ 4.0 of H-7-*syn* to 2 q, *J*(2-*endo*,7-*syn*) 7, *J*(3-*endo*,7-*syn*) 8, and *J*(3-*exo*,7-*syn*) 2 Hz
	H-7-*syn*	4.0	Collapse of br d at δ 5.60 of H-2-*endo* to br s, collapse of dd at δ 3.10 of H-3-*endo* to d, *J*(3-*endo*,3-*exo*) 17 Hz, and sharpening of br s at δ 7.48 of H-1
(9)	H-2-*endo*	4.60	Collapse of m at δ 3.46 of H-7-*syn*, m at δ 2.20 of H-3-*exo*, and m at δ 2.52 of H-3-*endo*
	H-3-*endo* and H-3-*exo*	2.35	Collapse of m at δ 3.46 of H-7-*syn* to br d, *J*(2-*endo*,7-*syn*) 8 Hz, and sharpening of br d at δ 6.40 of H-2-*endo* to d, *J*(2-*endo*,7-*syn*) 8 Hz
	Ph	7.19	Small changes at δ3.46 (H-7-*syn*)
	H-5 and H-6	5.70	Small changes at δ 3.46 (H-7-*syn*), δ 2.20 (H-3-*exo*), δ 2.52 (H-3-*endo*)
	H-7-*syn*	3.46	Collapse of br d at δ 4.60 of H-2-*endo* to br s and changes at δ 2.20 (H-3-*exo*) and δ 2.52 (*H*-3-*endo*)
(10)	H-3-*endo* and H-3-*exo*	2.86	Collapse of br t at δ 3.65 of H-7-*syn* to br s, sextet at δ 6.31 of H-5 to d, *J*(5,6) 6 Hz, and of sextet at δ 7.70 of H-6 to d, *J*(5,6) 6 Hz
	H-5	6.31	Collapse of sextet at δ 7.70 of H-6 to q, and changes at δ 2.86 (H-3-*endo* and H-3-*exo*)
	H-7-*syn*	3.65	Collapse of overlapping q at δ 2.86 of H-3-*endo* and H-3-*exo* to a q, and of d at δ 9.49 of H-8 to s

result from an *endo,endo* hydride shift in (12b), followed by Wagner–Meerwein rearrangement. This may further point to the stability of (12b) due to an additional contribution to its stabilisation from (15). Ions (13b) and (14b) cannot be derived directly from (4b) since



(15)

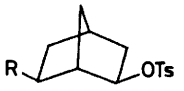
this would involve a forbidden 5,3-*exo,exo* hydride shift.[9]

Instead of the classical ions (3b), (4b), and (11b)—(14b), product formation may be explicable *via* the non-classical ions (7b), (16b), and (17b), for which (18b) is a composite.

The favouring of (4a) for product formation from (1a) and (1b) may well be because in (4a) the carbocation centre is remote from the electron-attracting carbonyl group. In (3a) there is possible backside overlap of the carbonyl with the vacant orbital of the carbocation centre. However, in (3b) this may be partially counteracted by the presence of the phenyl group leading to the formation of some product (1d). In (12b) the position of the carbonyl group is most unfavourable, and because (12b) is the major intermediate for product formation

from (1c), the extra stabilisation of (12b) provided by contributions from (15) must be of over-riding importance.

The results for the acetolysis of (1a) and the reaction of the iodides (1b) and (1c) with toluene-*p*-sulphonate ion all lead to products of predominant structural rearrangement. This may be contrasted with the studies of Grob [10] on the solvolysis of 6-*exo*-substituted 2-*exo*-norbornyl toluene-*p*-sulphonates (19) in which pre-



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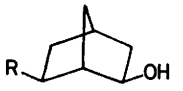

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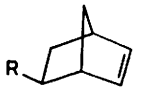

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dominantly unrearranged norbornanols (20) and norbornenes (21) resulted. It would therefore be a reasonable assumption that in ions (4b) and (12b), which lead to products, the stability of the lactone ring is greater than in the first-formed ion (3b), and must be a driving force in the rearrangement. The major product (8) has $\nu_{max.}$ for the γ-lactone carbonyl absorption in the i.r at 1 760 cm^{-1}, appreciably lower than the 1 800 and 1 790 cm^{-1} observed for products (1d) and (2c), respectively, which are produced in smaller quantities. This may indicate a greater stability for (8), and hence for intermediate (12b) from which it is derived.

EXPERIMENTAL

A mixture of norborn-5-en-2-*endo*-ylcarboxylic acid and its 2-*exo*-isomer was prepared by the method of Alder and Stein,[11] and using the procedure of van Tamelen and Shamma [12] converted into 6-*endo*-hydroxy-5-*exo*-iodonorborn-2-*endo*-ylcarboxylic acid γ-lactone (1b), m.p. 57—59 °C (lit.,[12] 58—59 °C). A mixture of 3-*exo*-phenylnorborn-5-en-2-*endo*-ylcarboxylic acid and its 2-*exo*-isomer were prepared by the method of Alder and Günzl [13] and similarly converted into 6-*endo*-hydroxy-5-*exo*-iodo-3-*exo*-phenylnorborn-2-*endo*-ylcarboxylic acid γ-lactone (1c), m.p. 124—126.5 °C (lit.,[14] m.p. 126—126.5 °C).

Reaction of 6-endo-*Hydroxy*-5-exo-*iodonorborn*-2-endo-*ylcarboxylic Acid γ-Lactone* (1b) *with Silver Toluene*-p-*sulphonate*.—A solution of the iodo-γ-lactone (1b) (2.0 g, 0.007 6 mol) in anhydrous actonitrile (11 ml) was added dropwise during 1 h to a well stirred solution of silver toluene-*p*-sulphonate [4] (4.0 g, 0.014 3 mol) in anhydrous acetonitrile (18 ml), cooled in an ice-bath to 5 °C and protected from light under a nitrogen atmosphere. 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 reaction mixture was then heated at reflux for 8 h, as a yellow precipitate of silver iodide gradually formed. The acetonitrile solution was decanted, the silver iodide precipitate washed with water (20 ml), and the washings added to the acetonitrile solution. The resultant solution was extracted with dichloromethane (4 × 30 ml), and the extracts combined and filtered through Celite. The filtrate was washed with water (2 × 30 ml), dried ($MgSO_4$), filtered, and the solvent evaporated to afford a yellowish oil (2.0 g) which by t.l.c. ($CHCl_3$, silica gel plates) showed a major component of R_F 0.31 and a minor component of R_F 0.44. Separation by p.l.c. ($CHCl_3$, 60 × 20 × 0.1 cm silica gel plates) afforded the the unreacted γ-iodolactone (1b) (0.5 g, 0.001 9 mol), m.p. 57—59 °C; and 7-syn-*hydroxy*-3-exo-*tosyloxynorborn*-6-exo-*ylcarboxylic acid γ-lactone* (2b) as a clear oil (1.30 g, 0.004 2 mol) which crystallised on standing to afford, after recrystallisation from light petroleum (b.p. 60—80 °C), white crystals, m.p. 103—105 °C (Found: C, 58.15; H, 5.3; $C_{15}H_{16}O_5S$ requires C, 58.45; H, 5.2%); δ (90 MHz, $CDCl_3$) 1.33 (br q, H-5-*endo*), 1.8 (m, H-2-*endo*, H-2-*exo*, H-5-*exo*), 2.46 (s, Me), 2.66 (m, H-6-*endo*, H-1, H-4), 4.69 (br q, H-3-*endo*), 4.99 (br s, H-7-*anti*), 7.36 (d, aromatic H), 7.79 (d, aromatic-H); *J*(*ortho,meta*) 8, *J*(2-*endo*,3-*endo*) 6, *J*(5-*endo*,6-*endo*) 6, and *J*(5-*endo*,6-*exo*) 14 Hz; $\nu_{max.}$ ($CHCl_3$) 1 790 (C=O) and 1 600 cm^{-1} (aromatic); *m/e* 308 ($M^{+\cdot}$)

Reaction of 6-endo-*Hydroxy*-5-exo-*iodo*-3-exo-*phenylnorborn*-2-endo-*ylcarboxylic Acid γ-Lactone* (1c) *with Silver Toluene*-p-*sulphonate*.—A solution of the γ-iodolactone (1c) (1.0 g, 0.002 9 mol) in anhydrous acetonitrile (20 ml) was added dropwise during 1 h to a well stirred solution of silver toluene-*p*-sulphonate (3.23 g, 0.011 6 mol) in anhydrous acetonitrile (30 ml), cooled in an ice-bath to 5 °C and protected from light under a nitrogen atmosphere. After completion of the addition, stirring was continued for a further 1 h as the temperature of the reaction mixture was allowed to rise to room temperature. The reaction mixture was then refluxed for 48 h, during which period a yellow precipitate of silver iodide gradually formed. The acetonitrile solution was decanted, the silver iodide precipitate washed with water (25 ml), and the washings added to the acetonitrile solution. This resultant solution was extracted with dichloromethane (6 × 20 ml), and the extracts combined and filtered through Celite. The filtrate was washed with water (2 × 20 ml), dried ($MgSO_4$), filtered, and the solvent evaporated to afford a yellowish brown oily residue (0.543 g). Separation by p.l.c. [ethyl acetate–light petroleum (b.p. 60—80 °C), (3 : 7), 60 × 20 × 0.1 cm silica gel plate] gave the following compounds: (i) 2-exo-*hydroxy*-4-*phenylnorborn*-5-*en*-7-anti-*ylcarboxylic acid γ-lactone* (8) (0.30 g, 1.41 m mol), R_F 0.43, as a white crystalline solid, m.p. 107—108 °C on recrystallisation from ethyl acetate–light petroleum (b.p. 60—80 °C) (1 : 9) (Found: C, 79.05; H, 5.6. $C_{14}H_{12}O_2$ requires C, 79.25; H, 5.55%); δ (90 MHz, $CDCl_3$) 2.4 (dm, H-3-*exo*), 3.10 (dd, H-3-*endo*), 4.0 (m, H-7-*syn*), 5.60 (br d, H-2-*endo*), 5.99 (m, H-5 and H-6), 7.50 (m, Ph and H-1); *J*(3-*endo*,3-*exo*) 17, *J*(3-*endo*,7-*syn*) 8, and *J*(2-*endo*,7-*syn*) 7 Hz; $\nu_{max.}$ ($CHCl_3$) 1 760 (C=O) and 1 650 cm^{-1} (CH=CH); *m/e* 212 ($M^{+\cdot}$), 183 ($M^{+\cdot}$—CHO), 167 ($M^{+\cdot}$—CO_2H), and 155 ($M^{+\cdot}$ — CHO — CO): (ii) 6-endo-*hydroxy*-3-exo-*phenyl*-5-exo-*tosyloxynorborn*-2-endo-*ylcarboxylic acid γ-lactone* (1d) (0.15 g, 0.39 mmol), R_F 0.35, as a white crystalline solid, m.p. 161—163 °C on recrystallisation from ethyl acetate–light petroleum (b.p. 60—80 °C) (1 : 9) (Found: C, 65.75; H, 5.3. $C_{21}H_{21}O_5S$ requires C, 65.45; H, 5.45%); δ (90 MHz, $CDCl_3$) 1.99 (br s, H-7-*syn* and H-7-*anti*), 2.47 (s, Me), 2.84 (br s, H-2-*exo* and H-3-*endo*), 3.15 (m, H-1 and H-4), 4.40 (br s, H-5-*endo*), 4.56 (d, H-6-*exo*), 7.19 (m, Ph), 7.35 (d, aromatic H), and 7.83 (d, aromatic H); *J*(1,6-*exo*) 1 and *J*(*ortho,meta*) 8 Hz; $\nu_{max.}$ ($CHCl_3$) 1 800 (C=O) and 1 600 cm^{-1} (aromatic); *m/e* 384 ($M^{+\cdot}$), 229 ($M^{+\cdot}$ — $C_7H_7SO_2$), and 212 ($M^{+\cdot}$ — $C_7H_7SO_2OH$): and (iii) 7-syn-*hydroxy*-5-endo-*phenyl*-3-exo-*tosyloxynorborn*-6-exo-*ylcarboxylic acid γ-lactone* (2c) (70.8 mg, 0.18 mmol), R_F 0.25, as white crystals, m.p. 130.5—132 °C on recrystallisation from ethyl acetate (Found: C, 65.8; H, 5.2. $C_{21}H_{21}O_5S$ requires C, 65.45; H, 5.45%); δ (90 MHz, $CDCl_3$) 1.96 (q, H-2-*endo*), 1.65 (m, H-2-*exo*), 2.42 (s, Me), 2.90 (m, H-4 and H-1), 3.18

(t, H-6-*endo*), 3.41 (d, H-5-*exo*), 4.08 (d, H-3-*endo*), 5.15 (br s, H-7-*anti*), 7.12 (d, aromatic H), 7.62 (d, aromatic H), and 7.30 (m, Ph); J(2-*endo*,3-*endo*) 6, J(2-*endo*,2-*exo*) 16, J(4,5-*exo*) 6, J(5-*exo*, 6-*endo*) 2, J(6-*endo*,7-*anti*) 2, and J(*ortho*, *m* = *eta*) 9 Hz; $\nu_{max.}$ ($CHCl_3$) 1 790 (C=O), 1 598 cm^{-1} (aromatic); *m/e* 384 ($M^{+\cdot}$), 229 ($M^{+\cdot} - C_7H_7SO_2$), and 212 ($M^{+\cdot} - C_7H_7SO_2OH$).

2-exo-*Hydroxy*-4-*phenylnorborn*-5-*en*-7-anti-*ylmethanol* (9).—A solution of the γ-lactone (8) (0.14 g, 0.66 mmol) in anhydrous ether (10 ml) was added dropwise during 0.5 h to a stirred suspension of lithium aluminium hydride [15] (0.1 g, 2.6 mmol) in anhydrous ether (40 ml). After stirring for a further 1.5 h, a saturated solution of ammonium chloride (15 ml) was added dropwise until a granular precipitate of inorganic salts had formed. The mixture was filtered, the filtrate dried ($MgSO_4$), and the solvent evaporated to afford the *diol* (9) as a colourless viscous liquid, solidifying on standing to afford crystals (0.114 g, 0.528 mmol), m.p. 75—77 °C on recrystallisation from light petroleum (b.p. 60—80 °C) (Found: C, 77.45; H, 7.2. $C_{14}H_{16}O_2$ requires C, 77.8; H, 7.4%); δ (90 MHz, $CDCl_3$) 2.20 (m, H-3-*exo*), 2.52 (m, H-3-*endo*), 3.46 (m, H-7-*syn*), 4.06 (q, H-8), 4.40 (br s, O*H*), 4.60 (d, H-2-*endo*), 5.70 (m, H-5 and H-6), 6.65 (s, H-1), and 7.19 (m, Ph); J(3-*exo*,3-*endo*) 18, J(3-*endo*,7-*syn*) 3, J(2-*endo*,-7-*syn*) 8, and J(8*a*,8*b*) 12 Hz; $\nu_{max.}$ ($CHCl_3$) 3 380 (OH) and 1 600 cm^{-1} (aromatic); *m/e* 216 ($M^{+\cdot}$), 199 ($M^{+\cdot}$ — OH), 183 ($M^{+\cdot} - CH_2OH$), and 168 ($M^{+\cdot}$ — OH — CH_2OH).

7-anti-*Formyl*-4-*phenylnorborn*-5-*en*-2-*one* (10).—To a well stirred solution of pyridinium dichromate [8] (3.2 g, 8.5 mmol) in anhydrous dimethylformamide (12 ml) was added a solution of the diol (9) (0.263 g, 1.22 mmol) in anhydrous dimethylformamide; the reaction was carried out under a nitrogen atmosphere in a three-necked flask (100 ml). After 5 h at room temperature the reaction mixture was diluted with water (120 ml) and then extracted with chloroform (6 × 30 ml). The combined extracts were washed with water (2 × 30 ml), dried ($MgSO_4$), and the solvent evaporated to give a yellow oil which crystallised on standing, and was recrystallised from ethyl acetate–light petroleum (b.p. 60—80 °C) (1 : 9) to afford the unsaturated ketoaldehyde (10) (0.19 g, 0.89 m mol) as white crystals, m.p. 133—135 °C (Found: C, 78.95; H, 5.6. $C_{14}H_{12}O_2$ requires C, 79.25; H, 5.65%); δ (90 MHz, $CDCl_3$) 2.86 (two overlapping q, H-3-*endo* and H-3-*exo*), 3.65 (t, H-7-*syn*), 6.31 (sextet, H-5), 7.43 (br s, Ph), 7.65 (s, H-1), 7.70 (sextet, H-6), and 9.49 (d, H-8); J(3-*endo*,7-*syn*) 4, J(3-*exo*,5-*exo*) 2, J(2-*endo*,7-*syn*) 4, J(7-*syn*,8) 1, and J(5,6) 6 Hz; $\nu_{max.}$ ($CHCl_3$) 1 710 (C=O) and 1 690 cm^{-1} (-CHO); *m/e* 212 ($M^{+\cdot}$), 183 ($M^{+\cdot}$ — CHO), and 155 ($M^{+\cdot}$ — CHO — CO).

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