o-Quinonoid Compounds. Part 17.[1] Evidence for *exo*-Selectivity in the 1,5-Sigmatropy of Acyl and Vinyl Groups

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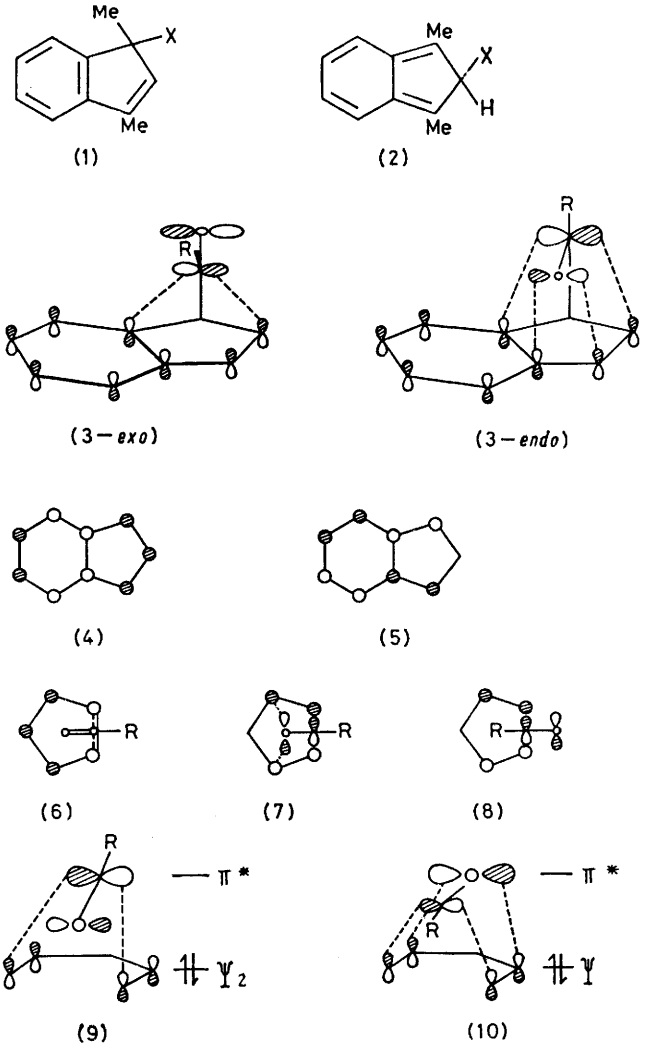
Arguments and experiments are presented which suggest that in the 1,5-sigmatropic shift of acyl groups in 1-acylindenes the acyl group prefers to adopt a transition state (t.s.) arrangement with the acyl-oxygen directed away from the indene ring (3-*exo*) rather than the arrangement (3-*endo*) with the acyl-oxygen over the indene ring. The order of migratory aptitude HCO $\gg$ Me_2CHCO > MeCO > Bu^tCO is consistent with this view, as is the slow racemisation of the cyclic ketones (11) and (18) constrained to adopt t.s. arrangements of the 3-*endo* type. Similar *exo*-selectivity in the migration of vinyl groups is indicated by comparing the racemisation rates of the olefins (20) and (21) at 250 °C; (21), which can give the transient and symmetric 2*H*-indene (23) *via* a t.s. of *exo*-type, racemises at least 50 times faster than (20), which must rearrange [to (22)] by a t.s. of *endo*-type.

In the 1,5-shift converting the optically active 1-acylindenes (1; X = acyl) into the symmetric 2*H*-indenes (2; X = acyl) the faster migration of acyl than alkyl groups, as well as the diverse migratory aptitudes of different acyl groups,[2] and the correlation of the migratory aptitude of *E*-substituted vinyl groups with the resonance electron-accepting ability of the *E*-substituent,[1] all favour involvement of the π-system of the migrating group in the rearrangement transition state (t.s.). This involvement could take the form of a *secondary interaction* between the HOMO of the styrene moiety and the π*-orbital of the migrating π-system [see (3)] which may be enhanced as reaction proceeds, and which accompanies *primary interaction* between the migrating σ-bond and the indene system. On the basis of this hypothesis migration *via* an *exo*-arrangement (3-*exo*) should be preferred to rearrangement *via* the *endo*-geometry (3-*endo*) in which antibonding secondary interactions are present. The Woodward-Hoffmann model for the t.s.'s of sigmatropic processes cannot be directly applied to 1,5-shift in indenes because of the nodal properties of ψ_4 [see (4)] and ψ_5 [see (5)] of the indenyl radical. However if the indene is regarded as a perturbed cyclopentadiene a similar *exo*-selectivity is predicted; interaction of the σ-orbital of the migrating 'acyl radical' with one of the degenerate HOMO's of the cyclopentadienyl radical is accompanied by interaction between the other cyclopentadienyl HOMO and the π*-orbital of a migrating 'radical' as in (7) and (8). Again the *endo*-arrangement (7) is destabilised by secondary interactions and the *exo*-arrangement (8) should be preferred. This conclusion is probably valid for all 1,5-shifts of unsaturated groups; interaction of ψ_2 of the pentadienyl radical with π* of a migrating acyl group is more favourable in the *exo*-geometry (9) than in the *endo*-arrangement (10).

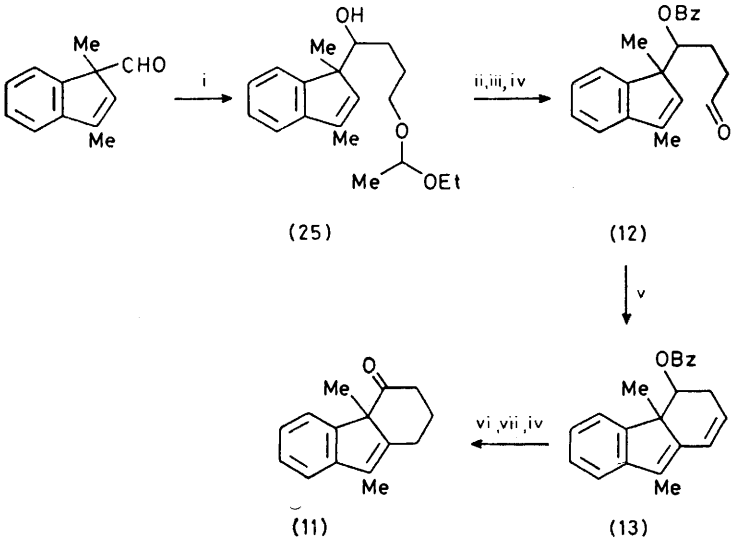
In search of the expected *exo*-selectivity we first compared the rearrangement rates (*k* racemisation) of the optically active indenes (1; X = CHO), (1; X = COMe), (1; X = $COPr^i$), and (1; X = $COBu^t$). In moving along this series the increasing bulk of the acyl substituent (R) was expected to lead to decreasing values of $k_{rac.}$ as an increasingly bulky group (R) is located over the indene 5-membered ring in the *exo*-t.s. arrangement (3-*exo*). In going to an *endo*-t.s. arrangement (3-*endo*) the group R moves into a sterically less demanding



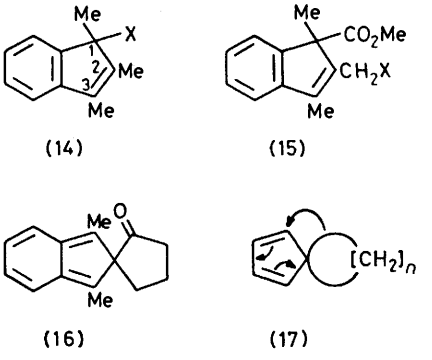
environment so that increasing the bulk of R should lead to increasing values of $k_{rac.}$ In agreement with both this interpretation and preferred *exo*-selectivity (1; X =

CHO) racemises *ca.* 10^3 times faster than (1; X = COMe) [2] and rearrangement of (1; X = $COBu^t$) is still slower ($k_{rac.}$ 13.4 × 10^{-5} s^{-1} at 191.7 °C in Ph_2O). However (1; X = $COPr^i$) rearranges *ca.* 2.6 times *faster* ($k_{rac.}$ 65.86 × 10^{-5} s^{-1} at 160 °C in Ph_2O) than (1; X = COMe). The small but unexpected rate increase in this case may be associated with a t.s. arrangement of the isopropyl group with its methine proton directed towards the indene rings so that steric interaction of this group with the indene moiety is no greater than that of the methyl group in the t.s. for rearrangement of (1; X = COMe). On the other hand steric factors will destabilise the ground state of (1; X = $COPr^i$) relative to the ground state of (1; X = COMe). An alternative explanation for much more rapid migration of the formyl than the other acyl groups would be that formyl migrates *via* an *exo*- and the other acyl groups *via* an *endo*-arrangement. This explanation fails, however, to account for the considerably *slower* migration of the pivaloyl group compared to the isobutyryl group (relative *k ca.* 40 at 190 °C). The data are most easily interpreted in terms of preferred *exo*-migration of all these acyl groups with the possible exception of the pivaloyl group. Slow migration of this group could be due to steric destabilisation of the *exo*-t.s. *or* to enforced *endo*-migration.

To obtain information on the rate retardation resulting from enforced *endo*-migration we sought to prepare the cyclohexanone derivative (11) in an optically active form. This was accomplished as shown in Scheme 1. The additional 3-carbon unit required for conversion of the optically active aldehyde (1; X = CHO) into (11) was provided by Eton's hydroxypropylation reagent (i) (Scheme 1).[3] Functional group manipulation then gave the aldehyde (12) which underwent smooth internal Prins reaction [4] and dehydration to form the required six-membered ring. Highly selective reduction of the disubstituted double bond in (13) was accomplished using Wilkinson's homogeneous hydrogenation catalyst.[5] Removal of the protecting benzoyl group with lithium aluminium hydride and oxidation of the resulting alcohol completed the synthesis of (11). Racemisation of (11) in diphenyl ether proceeded cleanly between 160 and 200 °C and afforded the following rate data [10^{-5} k/s^{-1} (T/°C)], 1.56 (160), 3.04 (170), 6.76 (180), 13.98 (190), 27.48 (200), $\Delta H^{\ddagger}$ = 29.62 ± 0.40 kcal mol^{-1}, and $\Delta S^{\ddagger}$ = −13.02 ± 0.88 cal K^{-1} mol^{-1}. The cyclic ketone (11) therefore racemises some 16.4 times more slowly than the acetyl derivative (1; X = COMe) at 160 °C and at a rate very similar to that of the pivaloyl derivative (1; X = $COBu^t$) at 190 °C. The rate retardation for racemisation of (11) is not associated with the presence of an alkyl substituent at C-2 in this case but absent for the derivatives (1). The 1,2,3-trimethyl-1-formylindene (14; X = CHO) was prepared from the optically active alcohol (15; X = OH) by reaction with hydrogen chloride in ether to give the chloride (15; X = Cl); reductive removal of the allylic chlorine atom and reduction of the ester group was achieved by treatment with lithium aluminium hydride in tetrahydrofuran, first at −20 °C and then at 60 °C. The resulting alcohol

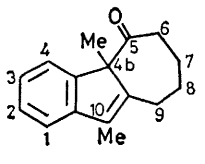


SCHEME 1 Reagents: i, $Li[CH_2]_3OCH(OEt)CH_3$; ii, $PhCOCl–C_5H_5N$; iii, H_3O^+; iv, $CrO_3·2py–CH_2Cl_2$; v, HCO_2H; vi, $(Ph_3P)_3RhCl$; vii, $LiAlH_4$



(14; X = CH_2OH) gave the desired aldehyde (14; X = CHO) on oxidation (CrO_3·2py–CH_2Cl_2). The alcohol (15; X = OH) was obtained by mild hydrolysis ($NaHCO_3$–H_2O) of the previously prepared formate ester.[4b] The aldehyde (14; X = CHO) racemised *ca.* 1.36 times faster (k 64.27 ± 0.22 s^{-1} in Ph_2O at 80 °C) than (1; X = CHO). This small acceleration may be due to decreasing steric interaction between the C-2 and C-3 methyl groups in the rearrangement t.s. which should resemble the 2*H*-indene intermediate. In interesting contrast a 2-methyl substituent markedly retards migration of trimethylsilyl and trimethylstannyl groups in simple indenes ($\Delta\Delta G^{\ddagger}$ *ca.* 4.5 kcal mol^{-1}).[6]

Although in accordance with preferred *exo*-migration of acyl groups the slow racemisation of (11) does not provide proof of this hypothesis. The greater angle strain of cyclopentanone than cyclohexanone will be reflected to some extent in the t.s. for rearrangement of (11) to the 2*H*-indene (16) and could account for slower rearrangement of (11) than (1; X = COMe). Such effects have been noted in ring-expansion rearrangements,[7] *e.g.* (17; $n = 4$) rearranges (17; arrows) 10^3 times faster than (17; $n = 5$). Accordingly the cyclohexanone (11) was reacted with diazomethane to give



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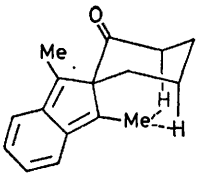
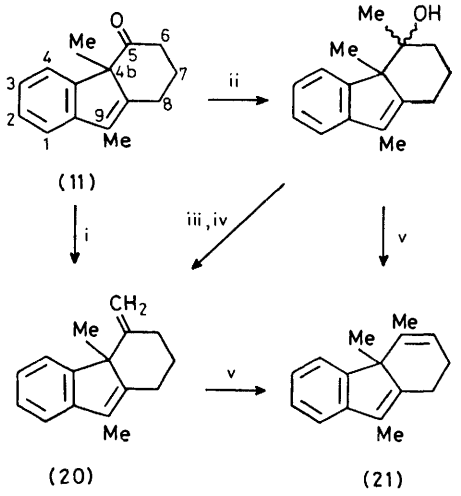


(19)

inter alia the cycloheptanone (18). Rearrangement of (18) should give the less strained cyclohexanone (19) so that if the angle strain were an important factor in determining rearrangement rate, racemisation of (18) would be fast. On the contrary (18) rearranged more slowly than (11) by a factor of 30 (k 7.48 × 10^{-5} s^{-1} at 230 °C in Ph_2O). The unexpectedly slow rearrangement of (18), like the lesser reactivity of cycloheptanone than cyclohexanone to nucleophilic attack, may be associated with bond-opposition strain (*I*-strain).[8] Alternatively, destabilisation of the 2*H*-indene (19) by steric interaction between a methyl group and the indicated axial hydrogens may be involved; such interaction is much reduced in (16) with its more nearly planar cyclopentanone ring.

The difference in racemisation rate constant between (11) and (18) clearly indicates the sensitivity of the 1,5-acyl shift to steric and related conformational factors and pointed the need for less equivocal evidence for the proposed *exo*-selectivity. This was sought in a comparison of $k_{rac.}$ values for the olefins (20) and (21); the former must migrate *via* an *endo*-arrangement to give the symmetric 2*H*-indene (22) but 1,5-shift in (21) would give (23) *via* an *exo*-t.s. arrangement. The olefins (20) and (21) were prepared from the cyclohexanone (11) as outlined in Scheme 2.

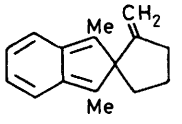
On heating in diphenyl ether at 250 °C the *endo*-cyclic olefin underwent fairly clean loss of optical activity ($k_{rac.}$ 6.6 × 10^{-5} s^{-1}). The formation of racemic (21) was accompanied by only a minor side reaction leading



(11) (20) (21)

SCHEME 2 Reagents: i, Ph_3PCH_2; ii, MeMgI; iii, $SOCl_2$–py; iv, 1,5-diazabicyclo[3.4.0]non-5-ene; v, *p*-$MeC_6H_4SO_3H$–benzene

to the naphthalene (24) (loss of CH_2!). Loss of optical activity for (21) was determined on starting material recovered (76%) by careful short-column chromatography [9] on silver nitrate silica. Racemisation of (20) under the same conditions proceeded very slowly ($k_{rac.}$ 0.135 × 10^{-5} s^{-1}) and the prolonged periods of heating required to effect noticeable loss of optical activity resulted in formation of the isomer (21) and the naphthalene (24); recovered olefin (20) (70% in one run and 25% yield in a second run) showed only a small reduction in optical activity (5% and 3%, respectively). Thus, whilst the $k_{rac.}$ value for (21) is regarded as reliable, that for (20) must be viewed as representing the maximum racemisation rate of (20) *via* 1,5-shift to the 2*H*-indene (22). The rate ratio of *ca.* 50 for racemisation of (21) and (20) corresponds to an activation energy difference of *ca.* 4 kcal mol^{-1} at 250 °C for the respective 1,5-shifts.



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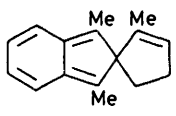

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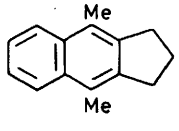

(24)

Heats of hydrogenation [10] indicate that methylenecyclohexane is less stable than 1-methylcyclohexene by 2.4 kcal mol^{-1} whereas methylene cyclopentane is less stable than 1-methylcyclopentene by 3.9 kcal mol^{-1}. If similar energy differences apply to (20) and (21), and

to (22) and (23), the activation energy for the (20) to (22) conversion would be *ca.* 1.5 kcal mol^{-1} greater than that for the (21) to (23) conversion. This leaves *ca.* 2.5 kcal mol^{-1} as the destabilisation associated with *endo*-rearrangement; since only a portion of the ground-state energy difference of 1.5 kcal mol^{-1} may be felt at the rearrangement t.s. this figure may be an underestimate.

Whilst we regard none of the evidence given herein as providing unequivocal proof, all our tests point to *exo*-selectivity in the 1,5-migration of unsaturated groups. The faster migration of *Z*- than *E*-olefins [1,11] and the slow rearrangement of alkoxycarbonyl and related groups [2] find ready explanation in terms of *exo*-selectivity.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. Unless otherwise specified n.m.r. spectra refer to solutions in deuteriochloroform measured with a Perkin-Elmer R 12 (60 MHz) or R 32 (90 MHz) spectrometer. Mass spectra were obtained with an A.E.I. MS 902 instrument. Where accurate mass measurement was used to establish molecular formulae the purity of the sample was checked by t.l.c. in more than one solvent system as well as by n.m.r. and i.r. spectroscopy. Optical rotations were obtained using a Perkin-Elmer 141 or Thorn type 243 polarimeter. Petroleum refers to light petroleum (b.p. 60—80 °C) and chromatography on silica to short-column chromatography [9] over Kieselgel G (Merck). Silica impregnated with 20% silver nitrate was prepared by adding silver nitrate (1 part) to a slurry of silica (5 parts) in water and heating the mixture in an oven at 140 °C overnight. After cooling the resulting cake was ground in a pestle and mortar and used in the usual way. Unless otherwise stated kinetic measurements were made as previously described.[2]

(+)-1,3-*Dimethyl*-1-*pivaloylindene* (1; X = COBu^t).—Lithium shot (435 mg) from lithium containing *ca.* 1% sodium was stirred in ether (19 ml) at −35 to −40 °C under an atmosphere of argon, and t-butyl chloride (5.78 g) in ether (6 ml) was added. After stirring at *ca.* −35 °C for 3 h most of the excess of lithium was dectanted and (+)-1-formyl-1,3-dimethylindene (1; X = C) [2] in a little ether was added after cooling to −60 °C. After stirring at −60 °C (30 min) and −30 °C (30 min) the reaction was quenched by addition of water with continued cooling at −30 °C. After warming to room temperature the product was washed with water, and the ether layer dried ($MgSO_4$) and evaporated, and the crude product chromatographed on silica in benzene–ether (9 : 1) to give *t-butyl*(1,3-*dimethylinden*-1-*yl*)*methanol* (295 mg) (Found: M^+, 230.166. $C_{16}H_{22}O$ requires *M*, 231.167), $\nu_{max.}$ 3 120—3 680; δ (60 MHz) 0.63 (9 H, s), 1.34 (3 H, s), 1.84br (1 H, s, OH), 2.09 (3 H, d, *J* 1.5 Hz), 3.76br (1 H, s, C*H*OH), 6.24 (1 H, q, *J* 1.5 Hz), and 7.23 (4 H, m, aromatic). Elution of this alcohol from the column followed elution of a supposed diastereoisomeric alcohol (55 mg), δ 0.74 (9 H, s), 1.38 (3 H, s), 1.68br (1 H, s, OH), 2.05 (3 H, d, *J* 1.5 Hz), 3.68br (1 H, s, C*H*OH), 6.02 (1 H, q, *J* 1.5 Hz), 7.18 (3 H, s, aromatic), and 7.47 (1 H, m, aromatic). Chromium trioxide (1.35 g), pyridine (2.12 g), and dichloromethane (36 ml) were stirred under nitrogen (15 min) at room temperature and the major product of the foregoing experiment (290 mg) in dichloromethane (2 ml) added and stirring continued (15 min). The product was diluted with ether and washed with sodium carbonate solution (×2), dilute hydrochloric acid (×2), saturated sodium hydrogen carbonate solution (×2), and water (×2). Evaporation of the dried ($MgSO_4$) ether layer and chromatography of the product on silica in benzene gave (−)-1,3-*dimethyl*-1-*pivaloylindene* (260 mg), m.p. 35—36 °C (from petroleum at −80 °C) (Found: C, 83.65; H, 8.65%; M^+, 228.151 4. $C_{16}H_{20}O$ requires C, 84.2; H, 8.8%; *M*, 228.151 2), $\nu_{max.}$ (film) 1 690 cm^{-1}; δ (60 MHz) 0.86 (9 H, s), 1.40 (3 H, s), 2.17 (3 H, d, *J* 1.5 Hz), 6.22 (1 H, q, *J* 1.5 Hz), and 7.27 (4 H, m, aromatic); $[\alpha]_D$ −23.96 (*c* 3.53, Ph_2O).

Thermolysis of (−)-1,3-*Dimethyl*-1-*pivaloylindene*.—The title compound (70.6 mg) was dissolved in diphenyl ether (2 ml) and heated in a constant temperature bath at 191.7 °C. Decrease of optical activity in the solution was followed as previously described [2] and gave a good first-order plot ($k_{rac.}$ 1.34 × 10^{-4} s^{-1}). After completion of the kinetic run a further quantity (60 mg) of the title ketone was added and the mixture heated at 196 °C (18 h). The product was chromatographed on silica in benzene–petroleum (9 : 1) to give 1,3-*dimethyl*-2-*pivaloylindene* (90 mg), m.p. 60—62 °C (from petroleum at −80 °C) (Found: C, 84.35; H, 9.0%; M^+, 228.151 9), $\nu_{max.}$ (Nujol) 1 669 cm^{-1}; δ (60 MHz) 1.2 (9 H, s), 1.35 (3 H, d, *J ca.* 7 Hz), 2.05 (3 H, d, *J* 2 Hz), 3.85 (1 H, qd, *J ca.* 7 and 2 Hz), and 7.27 (4 H, s, aromatic).

Hydroxypropylation of (+)-1-*Formyl*-1,3-*dimethylindene*.—Acetaldehyde ethyl 3-lithio-propyl acetal (30 ml, 30 mmol) was added to dry ether (80 ml) at 0 °C under nitrogen and a solution of (+)-1-formyl-1,3-dimethylindene (3.9 g, 22.7 mmol) in ether (10 ml) was added with stirring. After stirring at 0 °C (1.25 h) the mixture was poured onto half-saturated aqueous ammonium sulphate solution (100 ml), and the product extracted into ether. Evaporation of the dried ($MgSO_4$) ether extract and chromatography of the crude product (6.16 g) on silica (500 g) in ether–benzene (3 : 7) gave the hydroxyacetal (25) (4.2 g, 61%) as a mixture of diastereoisomers (Found: M^+ − EtOH, 258.162 5. $C_{17}H_{22}O_2$ requires *M*, 258.161 9), $\nu_{max.}$ (film) 3 460 cm^{-1}; δ (60 MHz) 2.4—2.9 (4 H, m, aromatic), 3.91 (1 H, m, olefinic), 5.37 (1 H, m), 6.2—6.8 (5 H, m), 7.26br (1 H, s, OH), 7.90 (3 H, d, *J* 1.5 Hz), and 8.1—9.0 (13 H, m); *m/e* 258, 214, 170, 155, 141, 128, and 115 (6.4, 3.1, 13, 11, 34, 44, and 30%); $[\alpha]_D^{24}$ +57.1° (*c* 1.097, $CHCl_3$).

Benzoylation and Hydrolysis of the Hydroxy-acetal (25).—A mixture of the diastereoisomeric hydroxy-acetals (25) (4.0 g, 13.2 mmol) and benzoyl chloride (2.5 g) was stirred in pyridine (50 ml) at 20 °C under nitrogen. After 30 min and 1 h further portions (2.5 and 2.4 g, respectively) of benzoyl chloride were added. After stirring for 16.5 h, sodium hydrogen carbonate solution was added and the mixture extracted with ether. Evaporation of the dried ($MgSO_4$) ether layer gave a crude product (9.13 g) which was dissolved in ethanol (350 ml) before addition of 350 ml of dilute hydrochloric acid (from 3.2 ml of conc. hydrochloric acid and 400 ml water) and stirring (1 h). The product was diluted with water, extracted into ether, and the ether layer evaporated. The crude product (7.27 g) was chromatographed on silica (250 g) in ether–benzene (3 : 7) to give (+)-4-*benzoyloxy*-4-(1,3-*dimethylinden*-1-*yl*)*butan*-1-*ol* (4.27 g, 96%) as a mixture of diastereoisomers (Found: M^+, 336.171 5. $C_{22}H_{24}O_3$ requires *M*, 336.172 5), $\nu_{max.}$ ($CHCl_3$) 3 490 and 1 715 cm^{-1}; δ (60 MHz) 8.2—7.9 (2 H, m, aromatic), 7.6—7.1 (7 H, m, aromatic), 6.13 (1 H, q, *J* 1.5 Hz), 5.52 (1 H, m), 3.41 (2 H, m), 3.16br (1 H, s, OH), 2.10 (3 H, d, *J* 1.5 Hz), and 1.36 (7 H, m); *m/e* 336, 214, 169, 141, 128,

and 105 (5, 18, 4, 11.5, 19, and 100%); $[\alpha]_D^{24}$ +23.7° (*c* 1.41, $CHCl_3$).

(+)-4-*Benzoyloxy*-4-(1,3-*dimethylinden*-1-*yl*)*butan*-1-*al* (12).—Chromium trioxide (1.074 g, 10.74 mmol) and pyridine (1.70 g, 21.5 mmol) were stirred in dichloromethane (60 ml) under nitrogen at 20 °C (15 min) before addition of the diastereoisomeric mixture of alcohols, prepared above (600 mg, 1.78 mmol), in dichloromethane (5 ml). After continued stirring (15 min) the product was diluted with ether and the ether layer washed with sodium hydrogen carbonate solution (×3), washed with 0.1M-hydrochloric acid, washed with sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated to give (+)-4-*benzoyloxy*-4-(1,3-*dimethylinden*-1-*yl*)*butan*-1-*al* (485 mg, 81%) as a mixture of diastereoisomers (Found: M^+, 334.156 3. $C_{22}H_{22}O_3$ requires *M*, 334.156 9), $\nu_{max.}$ (film) 1 720 and 1 605 cm^{-1}; δ (60 MHz) 9.57 (1 H, m, CHO), 8.3—7.9 (2 H, m, aromatic), 7.7—7.1 (7 H, m, aromatic), 6.16 (1 H, q, *J* 1.5 Hz), 5.56 (1 H, m), 2.29 (2 H, m), 2,13 (3 H, d, *J* 1.5 Hz), 1.63 (2 H, m), and 1.32 (3 H, s); *m/e* 334, 248, 212, 191, 169, 143, 128, and 105 (12, 24, 50, 15, 14, 33, 45, and 100%).

Preparation of 5-*Benzoyloxy*-4b,9-*dimethyl*-5,6-*dihydrofluorene* (13).—The foregoing (+)-benzoyloxy-aldehyde as a mixture of diastereoisomers (1.32 g, 3.96 mmol) was stirred in formic acid (50 ml, 98%) at 20 °C under nitrogen (1.5 h). The product was worked-up by addition of water and extraction into ether, followed by washing of the ether extract with water, washing with saturated sodium hydrogen carbonate solution, drying ($MgSO_4$), and evaporation of the ether to give a crude product (1.18 g) which was chromatographed on silica (120 g); elution with benzene–petroleum (7 : 3) gave first the major isomer of the (−)-5-*benzoyloxy*-4b,9-*dimethyl*-5,6-*dihydrofluorene* (453 mg, 36%) as colourless needles, m.p. 159—161 °C (from petroleum) (Found: C, 83.7; H, 6.45. $C_{22}H_{20}O_2$ requires C, 83.5; H, 6.3%), $\nu_{max.}$ (Nujol) 1 718 and 1 603 cm^{-1}; $\lambda_{max.}$ (EtOH) 289sh, 301, and 315sh nm (ε 15 117, 18 775, and 13 167); δ (60 MHz) 8.4—8.1 (2 H, m, aromatic), 7.65—6.85 (7 H, m, aromatic), 6.57 (1 H, dm, *J* 9 Hz), 5.78 (1 H, m, $W_{\frac{1}{2}}$ 21 Hz), 5.00 (1 H, dd, *J* 9 and 6 Hz), 2.60 (2 H, m), 2.08 (3 H, s), and 1.39 (3 H, s); *m/e* 316, 194, 179, 165, and 105 (14, 72, 63, 13, and 100%); $[\alpha]_D^{24}$ −373.7° (*c* 0.553, $CHCl_3$). Continued elution of the column gave a minor stereoisomer of the (−)-*benzoyloxyfluorene* (13) (133 mg, 10.5%) as a glass, $\nu_{max.}$ (film) 1 718 and 1 605 cm^{-1}; δ (60 MHz) 7.55—6.85 (9 H, m, aromatic), 6.63 (1 H, dm, *J* 11 Hz, olefinic), 5.9—5.45 (2 H, m), 2.61 (2 H, m), 2.12 (3 H, s), and 1.22 (3 H, s).

Homogeneous Hydrogenation of the Benzoyloxyfluorene (13).—The major stereoisomer of the benzoyloxyfluorene (13) (423 mg, 1.34 mmol) and tris(triphenylphosphine)-chlororhodium [5] (210 mg) in benzene (100 ml) were shaken in a hydrogen atmosphere at 20 °C (10 h). The crude product (735 mg), obtained by evaporation of solvent, was chromatographed on silica (45 g) in benzene–petroleum (7 : 3) to give the *dihydro-derivative* of the major benzoyloxyfluorene (13) (413 mg, 97%) as colourless needles, m.p. 134—137 °C (from chloroform–ethanol) (Found: C, 82.75; H, 6.6. $C_{22}H_{22}O_2$ requires C, 83.0; H, 6.9%), $\nu_{max.}$ (Nujol) 1 713 cm^{-1}; $\lambda_{max.}$ (EtOH) 261.5, 284.5sh, and 293.5 nm (ε 12 008, 2 573, and 858); δ (60 MHz) 8.4—8.1 (2 H, m, aromatic), 7.7—6.85 (7 H, m, aromatic), 4.47 (1 H, m), 2.9—1.2 (6 H, m), 2.04 (3 H, s), and 1.42 (3 H, s); *m/e* 318, 196, 181, and 105 (18, 67, 38, and 100%); $[\alpha]_D^{24}$ −201.5° (*c* 0.548, $CHCl_3$).

The minor isomer of the (−)-benzoyloxyfluorene (13) (130 mg, 0.412 mmol) and tris(triphenylphosphine)chlororhodium (65 mg) in benzene (20 ml) were shaken in hydrogen at 20 °C (44 h). Chromatographic isolation on silica in benzene–petroleum (4 : 1) gave the *dihydro-derivative* of the minor benzoyloxyfluorene (13) (114 mg, 87%) as a glass (Found: M^+, 318.160 9. $C_{22}H_{22}O_2$ requires *M*, 318.161 9), $\nu_{max.}$ (Nujol) 1 715 cm^{-1}; δ (60 MHz) 7.55—6.8 (9 H, m, aromatic), 5.73 (1 H, m), 3.1—2.4 (6 H, m), 2.11 (3 H, s), and 1.33 (3 H, s); *m/e* 318, 196, 181, and 105 (13, 59, 41, and 100%). In subsequent experiments the major and minor stereoisomers of benzoyloxyfluorene (13) were hydrogenated together over 2.5 days in the same way as described above.

Reduction of the Dihydro-derivative of the Benzoyloxyfluorene (13) *with Lithium Aluminium Hydride*.—The major stereoisomer of the dihydro-derivative of (13) (386 mg, 1.21 mmol) in ether (30 ml) was stirred under nitrogen at −20 °C and lithium aluminium hydride (92 mg, 2.42 mmol) added, and stirring continued at −20 °C (30 min). After warming to 20 °C during 30 min the reaction mixture was quenched by careful addition of water; after dilution with ether the organic layer was washed with water, dried ($MgSO_4$), and evaporated. The crude product (371 mg) was chromatographed on silica (45 g) in benzene–ether (9 : 1) to give one stereoisomer of 4b,9-dimethyl-5,6,7,8-tetrahydrofluoren-5-ol (247 mg, 95%) as a colourless oil (Found: M^+, 214.134 9. $C_{15}H_{18}O$ requires *M*, 214.135 7), $\nu_{max.}$ (film) 3 420 cm^{-1}; $\lambda_{max.}$ (EtOH) 262.5 nm (ε 11 500); δ (60 MHz) 7.7—7.0 (4 H, m, aromatic), 3.1—2.4 (2 H, m), 2.3—1.4 (6 H, m), 2.01 (3 H, s), and 1.19 (3 H, s); *m/e* 214, 196, 181, 170, and 157 (63, 35, 28, 48, and 100%); $[\alpha]_D^{24}$ +9.4° (*c* 8.623, $CHCl_3$).

The minor stereoisomer of the dihydro-derivative of (13) was similarly converted into a minor second stereoisomer of 4b,9-dimethyl-5,6,7,8-tetrahydrofluoren-5-ol (100% yield), which is an oil, δ (60 MHz) 7.45—7.1 (4 H, m, aromatic), 4.29 (1 H, m), 3.0—1.4 (6 H, m), 2.05 (3 H, s), 1.25 (3 H, s), and 1.01br (1 H, s, OH). For preparative purposes the foregoing reductions were performed on a mixture of the major and minor stereoisomers of the fluorene (13).

4b,9-*Dimethyl*-7,8-*dihydrofluoren*-5(6H)-*one* (11).—The foregoing major stereoisomer of 4b,9-dimethyl-5,6,7,8-tetrahydrofluoren-5-ol (222 mg, 1.04 mmol) was oxidised with chromium trioxide (622 mg, 6.22 mmol) and pyridine (984 mg, 12.44 mmol) in dichloromethane (50 ml) during 15 min. The product was diluted with ether and the organic layer washed with saturated sodium hydrogen carbonate solution (×3), washed with 0.1 M-hydrochloric acid, washed with saturated sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated to give (+)-4b,9-*dimethyl*-7,8-*dihydrofluoren*-5(6H)-*one* (11) (190 mg, 86%) as a colourless oil (Found: M^+, 212.119 8. $C_{15}H_{16}O$ requires M, 212.120 1), $\nu_{max.}$ (film) 1 713 cm^{-1}; $\lambda_{max.}$ 254, 268, and 294 nm (ε 7 289, 7 357, and 1 976); δ (60 MHz) 7.7—7.45 (1 H, m, aromatic), 7.4—7.1 (3 H, m, aromatic), 3.05—1.2 (6 H, m), 1.99 (3 H, d, *J* 1 Hz), and 1.44 (3 H, s); *m/e* 212, 197, 169, 157, 141, and 115 (97, 21, 12, 100, 43, and 14%); $[\alpha]_D^{24}$ +257.3° (*c* 0.74, $CHCl_3$).

The minor stereoisomer of 4b,9-dimethyl-5,6,7,8-tetrahydrofluoren-5-ol was similarly converted into the ketone (11) (93% yield). In preparative experiments the major and minor stereoisomers were oxidised together without loss of yield.

4b,10-*Dimethyl*-6,7,8,9-*tetrahydrocyclohept*[a]*inden*-

5-*one* (18).—The foregoing cyclohexanone (610 mg) in methanol (45 ml) was treated with an excess of ethereal diazomethane at 0—5 °C (36 h). Fresh ethereal diazomethane was added and the mixture maintained at 0—5 °C (12 h). The crude product (690 mg), obtained by evaporation of solvent, was chromatographed on silica (100 g) in benzene. After an initial fraction lacking carbonyl absorption (45 mg) benzene eluted 4b,10-*dimethyl*-6,7,8,9-*tetrahydrocyclohept*[a]*inden*-5(6H)-*one* (18) (135 mg) (Found: M^+, 226.135 1. $C_{16}H_{18}O$ requires M, 226.135 7), $\nu_{max.}$ (Nujol) 1 703 cm^{-1}; δ (60 MHz) 7.2 (4 H, m, aromatic), 2.7—3.0 (2 H, m, CH_2CO), 2.3—1.1 [6 H, complex m, $(CH_2)_3$], 2.1 (3 H, s), and 1.38 (3 H, s); *m/e* 226, 198, 183, 170, 169, 155, 142, and 141 (100, 29, 90, 36, 31, 63, 31, and 42%); $[\alpha]_D^{30}$ −77.7° (*c* 1.13, $CHCl_3$). Further elution of the column gave recovered starting material (50 mg) and an isomeric cycloheptanone (340 mg), tentatively identified as 4b,10-*dimethyl*-5,7,8,9-*tetrahydrocyclohept*[a]*inden*-6-*one* (Found: M^+, 226.136 4), $\nu_{max.}$ (film) 1 700 cm^{-1}; δ (60 MHz) 7.21 (4 H, s, aromatic), 2.90 (1 H, d, *J* 13 Hz), 2.48 (1 H, d, *J* 13 Hz), 1.5—3.0 [6 H, complex m, $(CH_2)_3$], 2.01 (3 H, s), and 1.22 (3 H, s); *m/e* 212, 157, 156, 155, 141, and 94 (58, 100, 68, 41, 46, and 42%); $[\alpha]_D^{40}$ +108.48 (*c* 1.25, Ph_2O).

Thermolysis of the Ketone (18).—The title compound (47.7 mg) in diphenyl ether (2 ml) was heated at 230 °C for 184 min. Polarimetric readings taken at intervals during this period yielded a good first-order plot and a $k_{rac.}$ value of 7.48 × 10^{-5} s^{-1}. The cycloheptanone (18) was recovered by chromatography on silica in benzene; its optical rotation $[\alpha]_D^{30}$ −33.55° (*c* 1.21, $CHCl_3$) yields a $k_{rac.}$ value of 7.49 × 10^{-5} s^{-1}. The major product of the reaction of diazomethane with (11) failed to show any loss in optical activity after heating in diphenyl ether at 230 °C (2 h).

2-*Hydroxymethyl*-1-*methoxycarbonyl*-1,3-*dimethylindene*.—(+)-2-Formyloxymethyl-1-methoxycarbonyl-1,3-dimethylindene (65% pure, 869 mg),[4b] sodium hydrogen carbonate (850 mg), water (4 ml), and methanol (20 ml) were boiled under reflux in a nitrogen atmosphere (70 min). After removal of solvents *in vacuo* the product was distributed between water and ether, and the ether layer washed with water, dried ($MgSO_4$), and evaporated, and the crude product (700 mg) chromatographed on silica (45 g) in ether–benzene (1 : 4) to give (+)-2-*hydroxymethyl*-1-*methoxycarbonyl*-1,3-*dimethylindene* (389 mg) as a colourless oil (Found: M^+, 232.108 9. $C_{14}H_{16}O_3$ requires M, 232.109 9), $\nu_{max.}$ (film) 3 440 and 1 728 cm^{-1}; δ (60 MHz) 7.6—7.1 (4 H, m, aromatic), 4.54 (1 H, d, *J* 13 Hz), 4.41 (1 H, d, *J* 13 Hz), 3.54 (3 H, s), 2.89br (1 H, s, OH), 2.10 (3 H, s), and 1.59 (3 H, s); *m/e* 232, 202, 173, 155, 143, and 128 (62, 88, 100, 75, 59, and 31%).

1-*Hydroxymethyl*-1,2,3-*trimethylindene*.—(+)-2-Hydroxymethyl-1-methoxycarbonyl-1,3-dimethylindene (250 mg, 1.08 mmol) was dissolved in dry ether (50 ml) and hydrogen chloride bubbled through the solution (10 min). After 1 h at 20 °C the solution was evaporated under reduced pressure to give crude (+)-2-chloromethyl-1-methoxycarbonyl-1,3-dimethylindene (253 mg), $\nu_{max.}$ (film) 1 728 cm^{-1}; δ (60 MHz) 7.6—7.1 (4 H, m, aromatic), 4.50 (2 H, s), 3.57 (3 H, s), 2.18 (3 H, s), and 1.66 (3 H, s). This crude product (250 mg, 1.0 mmol) in dry tetrahydrofuran (30 ml) was stirred under nitrogen at −20 °C, lithium aluminium hydride (115 mg, 3.0 mmol) was added, and stirring continued for 1 h at −20 °C. After warming to 20 °C during 10 min the mixture was boiled under reflux (30 min) and quenched by careful addition of water. The mixture was diluted with ether and the ether layer washed with dilute hydrochloric acid, washed with water, dried ($MgSO_4$), and evaporated to give a crude product (194 mg) which was chromatographed on silica (40 g) in benzene–ether (9 : 1) to give (+)-1-*hydroxymethyl*-1,2,3-*trimethylindene* (14; X = CH_2OH) (149 mg, 74%) as a colourless oil (Found: M^+, 188.119 8. $C_{13}H_{16}O$ requires M, 188.120 1), $\nu_{max.}$ (film) 3 390 cm^{-1}; δ (60 MHz) 7.2 (4 H, m, aromatic), 3.72 (1 H, d, *J* 11 Hz), 3.50 (1 H, d, *J* 11 Hz), 2.00 (3 H, q, *J* 0.5 Hz), 1.83 (3 H, q, *J* 0.5 Hz), 1.33br (1 H, s, OH), and 1.14 (3 H, s); *m/e* 188, 157, 142, 129, and 115 (55, 100, 64, 32, and 19%).

(+)-1-*Formyl*-1,2,3-*trimethylindene*.—(+)-1-Hydroxymethyl-1,2,3-trimethylindene (150 mg, 0.8 mmol) was oxidised with chromium trioxide (480 mg, 4.8 mmol) and pyridine (759 mg, 9.6 mmol) in dichloromethane (60 ml) during 30 min and the product worked up by dilution with ether, and washing the ether layer (i) with dilute sodium hydroxide solution, (ii) with dilute hydrochloric acid, and (iii) with water. Evaporation of the dried ($MgSO_4$) layer gave a crude product (172 mg) which was chromatographed on silica (40 g) in benzene to give (+)-1-*formyl*-1,2,3-*trimethylindene* (14; X = CHO) (89 mg, 62%) as a colourless oil (Found: M^+, 186.104 1. $C_{13}H_{14}O$ requires M, 186.104 4), $\nu_{max.}$ (film) 1 718 cm^{-1}; δ (90 MHz) 8.32 (1 H, s, CHO), 7.5—7.1 (4 H, m, aromatic), 2.13 (3 H, q, *J* 0.5 Hz), 1.87 (3 H, q, *J* 0.5 Hz), and 1.43 (3 H, s); *m/e* 186, 158, 143, 128, and 115 (35, 82, 100, 41, and 29%); $[\alpha]_D^{24}$ +166.2 (*c* 1.22, $CHCl_3$).

4b,9-*Dimethyl*-5-*methylene*-5,6,7,8-*tetrahydrofluorene* (20).—Butyl-lithium (128 mg, 2.0 mmol) in hexane was syringed into a slurry of methyltriphenylphosphonium bromide (714 mg, 2.0 mmol) in ether (30 ml) at 0 °C under nitrogen and the yellow solution stirred at 0 °C (2 h) before addition of ketone (11) (109 mg, 0.514 mmol) in ether (5 ml). The mixture was stirred at 20 °C (1 h), boiled under reflux (1 h), and quenched by addition of water. Evaporation of the dried ($MgSO_4$) ether layer and chromatography of the crude product (290 mg) on silica (40 g) in benzene–petroleum (1 : 9) gave 4b,9-*dimethyl*-5-*methylene*-5,6,7,8-*tetrahydrofluorene* (20) (45 mg, 42%) as a colourless oil (Found: M^+, 210.140 2. $C_{16}H_{18}$ requires M, 210.140 8), $\nu_{max.}$ (film) 1 650, 1 637, and 1 608 cm^{-1}; $\lambda_{max.}$ (EtOH) 267.5, 287sh, and 295 nm (ε 10 227, 2 576, and 859); δ (90 MHz) 7.5—7.0 (4 H, m, aromatic), 4.77 (1 H, m), 4.53 (1 H, m), 2.9—1.9 (5 H, m), 1.98 (3 H, d, *J* 1.5 Hz), 1.35 (3 H, s), and 1.5—1.1 (1 H, m); *m/e* 210, 195, 180, 167, 152, 141, and 115 (40, 100, 20, 21, 18, 12, and 12%); $[\alpha]_D^{24}$ +437.8° (*c* 0.673, $CHCl_3$).

4b,5,9-*Trimethyl*-5,6,7,8-*tetrahydrofluoren*-5-*ol*.—To the (+)-ketone (11) (490 mg, 2.3 mmol) in ether (50 ml) at 20 °C under nitrogen was added, with stirring, methylmagnesium iodide [8 ml of a solution prepared from magnesium (600 mg) and methyl iodide (3.5 g) in ether (40 ml)]. Further 8 ml portions of the Grignard reagent were added after 45 min and 8.5 h stirring of the reaction mixture. After a further 1.5 h the reaction mixture was treated with saturated ammonium chloride solution and the ether layer washed with water, dried ($MgSO_4$), and evaporated to give a crude product (518 mg) which was chromatographed on silica (50 g) in benzene–ether (19 : 1) to give the first recovered starting material (48 mg). Continued elution of the column gave 4b,5,9-*trimethyl*-5,6,7,8-*tetrahydrofluoren*-5-*ol* (411 mg, 87%) as a colourless oil. (Found: M^+, 228.150 7. $C_{16}H_{20}O$ requires M, 228.151 4), $\nu_{max.}$ (film) 3 500 and 1 587 cm^{-1}; δ (60 MHz) 7.7—7.0 (4 H, m, aromatic), 1.98br (3 H,

s), 2.9—1.3 (7 H, m), 1.28 (3 H, s), and 0.60 (3 H, s); *m/e* 228, 210, 195, 170, 157, and 141 (31, 16, 30, 100, 52, and 18%).

4b,5,9-*Trimethyl*-7,8-*dihydrofluorene* (21).—The foregoing alcohol (125 mg, 0.55 mmol), *dry* toluene-*p*-sulphonic acid (20 mg), and benzene (16 ml) were boiled under reflux (1.5 h). After addition of toluene-*p*-sulphonic acid (20 mg) and continued boiling under reflux (0.5 h), the product was washed with sodium hydrogen carbonate solution and the benzene solution dried ($MgSO_4$) and evaporated to give a crude product (123 mg). Chromatography on silica (50 g) in benzene–petroleum (1 : 39) gave 4b,5,9-*trimethyl*-7,8-*dihydrofluorene* (21) (76 mg, 65%) as a low-melting solid (Found: M^+, 210.140 6. $C_{16}H_{18}$ requires M, 210.140 8), $\nu_{max.}$ (film) 1 473 and 1 453 cm^{-1}; $\lambda_{max.}$ (EtOH) 264.5 and 287sh nm (ε 10 093 and 1 546); δ (90 MHz) 7.55—7.0 (4 H, m, aromatic), 5.29 (1 H, m, olefinic), 2.95—2.1 (4 H, m), 2.03 (3 H, s), 1.98 (3 H, m), and 1.35 (3 H, s); *m/e* 210, 195, 180, 165, and 153 (78, 100, 31, 34, and 7%); $[\alpha]_D^{24}$ +84.4° (*c* 1.257, $CHCl_3$). This endocyclic olefin was also formed (59% yield) from the exocyclic olefin (20) (29 mg) by refluxing in boiling benzene (3 ml) containing *ca.* 3 mg of toluene-*p*-sulphonic acid (1 h) and isolating the product by chromatography on 20% silver nitrate on silica (60 g) in benzene–petroleum (1 : 4).

Alternative Preparation of 4b,9-*Dimethyl*-5-*methylene*-5,6,7,8-*tetrahydrofluorene* (20).—4b,5,9-Trimethyl-5,6,7,8-tetrahydrofluoren-5-ol (270 mg, 1.18 mmol) and purified thionyl chloride (4 ml) were stirred in pyridine (20 ml) at 0 °C in a nitrogen atmosphere (1 h). The product was diluted with ether and washed with dilute hydrochloric acid, washed with water, washed with saturated sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated to give a crude chloride (235 mg, 81%), δ (60 MHz) 7.9—7.6 (1 H, m, aromatic), 7.4—7.0 (3 H, m, aromatic), 3.0—1.2 (6 H, m), 1.99 (3 H, s), 1.44 (3 H, s), and 1.01 (3 H, s). This crude chloride (190 mg, 0.77 mmol) and 1,5-diazabicyclo[4.3.0]non-5-ene [12] (1 ml) were stirred at 130 °C under nitrogen (16.25 h). The cooled product was diluted with ether and the ether solution washed with dilute hydrochloric acid, washed with saturated sodium hydrogen carbonate solution, dried ($MgSO_4$), and evaporated to give a crude product (160 mg) which was chromatographed on 20% silver nitrate–silica (60 g) in benzene–petroleum (1 : 1) to give the olefin (20) (117 mg, 73%); $[\alpha]_D^{24}$ +437.8° (*c* 0.673, $CHCl_3$).

Thermolysis of the Olefin (21).—The olefin (38 mg) was sealed in a Pyrex tube under nitrogen and heated at 250 °C (4 h 12 min). The product was chromatographed on 20% silver nitrate–silica (60 g) in benzene–petroleum (1 : 4) to give the pure olefin (21) (29 mg), $[\alpha]_D^{24}$ +31.02° (*c* 0.953, $CHCl_3$).

Thermolysis of the Olefin (20).—(*a*) The racemic olefin (20) (45 mg) was sealed in a Pyrex tube under nitrogen and heated at 250 °C (14 h). The product was chromatographed on 20% silver nitrate–silica in benzene–petroleum (1 : 1) to give the *naphthalene* (24) (7 mg) as colourless needles, m.p. 73—77 °C (from methanol) (Found: M^+, 196.124 4. $C_{15}H_{16}$ requires M, 196.125 2), δ (90 MHz) 8.1—7.85 (2 H, m, aromatic), 7.55—7.30 (2 H, m, aromatic), 3.06 (4 H, t, *J* 5 Hz), 2.57 (6 H, s), 2.22 (1 H, d, *J* 5 Hz), and 2.07 (1 H, d, *J* 5 Hz); *m/e* 196, 181, 178, and 165 (100, 100, 17, and 33%). Continued elution of the column gave the endocyclic olefin (21) (20 mg).

(*b*) The (+)-olefin (20) was sealed in a Pyrex tube under nitrogen and heated at 250 °C for 8 h 26 min, and the products isolated as in experiment (*a*) above to give recovered olefin (20) (14 mg), $[\alpha]_D^{24}$ +415.8° (*c* 0.473, $CHCl_3$). The experiment was repeated with 40 mg of olefin (20) to give recovered olefin (20) (10 mg), $[\alpha]_D^{24}$ +425° (*c* 0.495, $CHCl_3$), as well as the naphthalene (24) and the endocyclic olefin (21).

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