o-Quinonoid Compounds. Part 15.[1] Rapid Formyl Migration in 1-Formylindenes; Evidence for Concertedness and Exclusive 1,5-Sigmatropy

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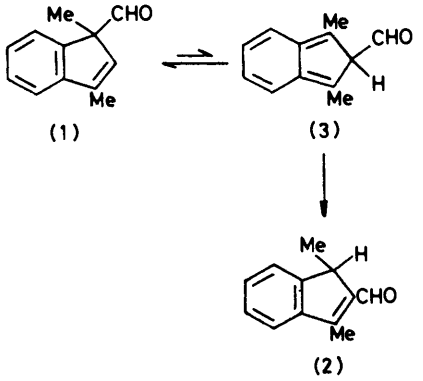
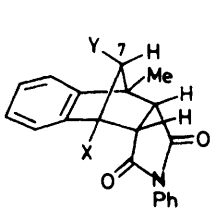
1-Formyl-3-methoxymethyl-1-methylindene (6) and 1-deuterioformyl-2-formyl-1,3-dimethylindene (15) have been prepared in optically active form. Interconversion of (6) and 1-formyl-1-methoxymethyl-3-methylindene (8) at 80 °C proceeds with ≥ 95% retention of optical activity over 100 half-lives. Racemisation of (15) is twice as fast as its conversion to 2-deuterioformyl-1-formyl-1,3-dimethylindene (17) showing that each act of racemisation involves formation of the symmetric 2*H*-indene intermediate (16) in which there is a 50% chance of CHO–CDO exchange.

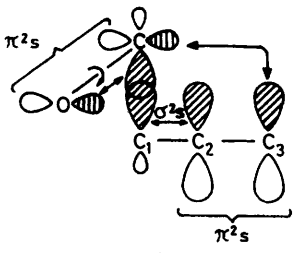
We have shown that 1-formyl-1,3-dimethylindene (1) rearranges to 2-formyl-1,3-dimethylindene (2) on heating and have proposed a mechanism for the reaction involving 1,5-formyl migration to give the isoindene (3) which gives (2) by 1,5-hydrogen shift (Scheme 1). In support of this mechanism the 2*H*-indene (3) could be trapped as a mixture of the *N*-phenylmaleimide adduct (4) and its 7-epimer.[2] However, at 80 °C the rate of racemisation of optically active (1) was $>10^2$ times faster than the rate of trapping of (3) with *N*-phenylmaleimide (3 mol equiv.) and 10^4 times faster than the rate of formation of the 2-isomer (2). The rate of racemisation of (1) was also 10^3 times faster than racemisation of 1-acetyl-1,3-dimethylindene. These observations raised doubts that racemisation of (1) involved *only* concerted 1,5-formyl migration to the symmetric isoindene (3). Conceivable alternative routes for racemisation of optically active (1) are shown in Scheme 2.† The (−)-enantiomer could be formed by a suprafacial 1,3-formyl shift occurring by the concerted-forbidden pathway[3] or the $\pi^2s + \pi^2s + \sigma^2s$ process involving the π-system of the migrating group pictured in (5). Alternatively (−)-(1) could be formed by homolysis to an indenyl radical and a formyl radical followed by recombination of the radicals at C-3 on the *same* face of the indene moiety. Combination of the formyl radical at C-1 on the *opposite* face of the indenyl radical would also give (−)-(1). This could be accomplished by a 180° rotation of the indenyl radical out of the plane of the paper (Scheme 2); such combination is a likely consequence of racemisation *via* a radical pair; it is known[4] that for caged α-phenethyl radical pairs 180° out-of-plane rotation of one radical relative to the other occurs with a rate constant 15 times greater than that for combination of the radicals. The degree of retention of configuration observed for migrating α-phenethyl groups in the Stevens rearrangement depends critically on the viscosity of the solvent.[5] Combination of the two radicals at C-2 of the indenyl radical giving the 2*H*-indene (3) is unlikely. The HOMO of the indenyl radical carries a node at C-2 so that C-1–C-2–C-3 of the indenyl system resembles the allyl system. This resemblance is confirmed by the e.s.r. spectrum of the indenyl radical.[6] Thus only concerted racemisation of



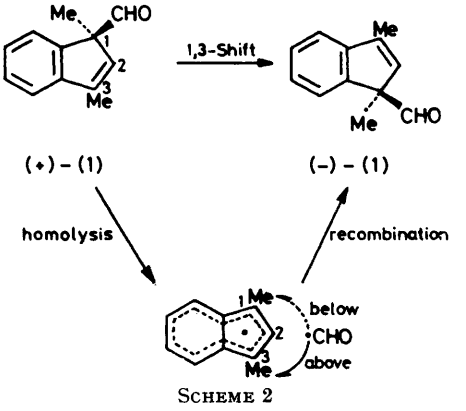
Scheme 1



(4) X = Me, Y = CHO
(13) X = CH_2OMe, Y = COPh
(14) X = CH_2OMe, Y = CHO



(5)

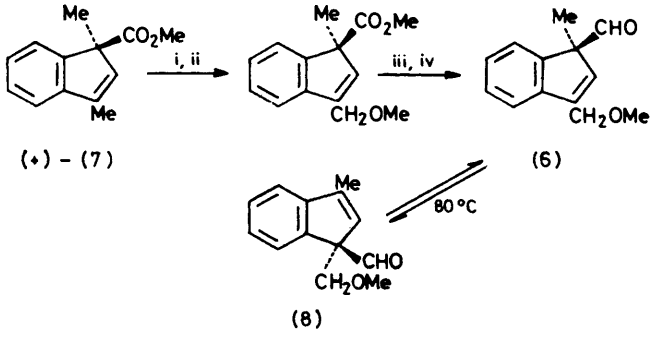


Scheme 2

† The assignment of absolute configuration is arbitrary throughout this paper.

(+)-(1) by two 1,5-shifts would be expected to involve just one face of the indene system and temporary location of the formyl group at C-2 of the indene. Possible involvement of ion-pair intermediates in the racemisation of (1) appears to be discounted by the small solvent-rate effects observed.

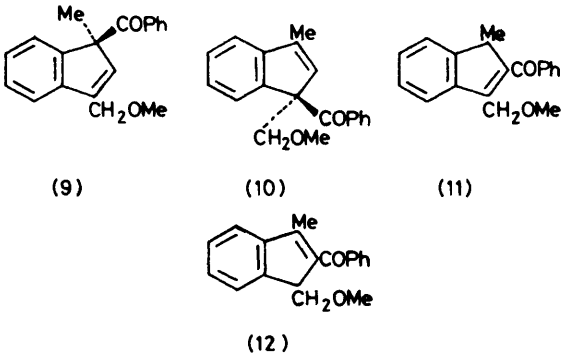
To establish that the formyl group remains on one face of the indene system we prepared the unsymmetrically substituted indene (6) from the optically active ester (7) (Scheme 3 *). Interconversion of (6) and its isomer (8) would be stereospecific if the rearrangement mechanism involved either two 1,5-shifts and a 2*H*-indene intermediate, or a direct 1,3-shift. Intervention of a radical pair as in Scheme 2 would however provide opportunity for formation of the enantiomers of (6) and (8). After heating for 3 h in boiling benzene, (6) was cleanly converted into a mixture of (6) and (8) in which the latter predominated (*ca.* 73%). Based on the initial



SCHEME 3

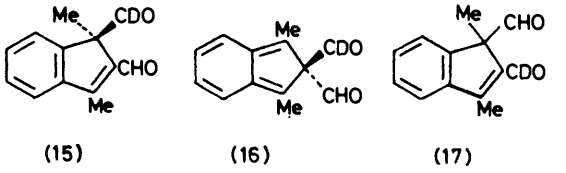
Reagents: i, *N*-bromosuccinimide; ii, MeOH–$CaCO_3$; iii. $LiAlH_4$; iv, CrO_3·2py

rate of isomerisation of (6) to (8) (n.m.r.) all the (6) present had undergone rearrangement yet careful chromatographic separation of the mixture gave (6) with its optical activity unchanged ($[\alpha]_D$ +123.7°). Moreover, when the product (8) ($[\alpha]_D$ − 65.7°) was heated at 80 °C (3.5 h) the isomer (6) reclaimed had lost little optical activity ($[\alpha]_D$ +122.9°). Even after heating a mixture of (6) and (8) for 48 h [*ca.* 100 half-lives for the conversion of (6) to (8)] the recovered isomers each retained ≥95% of their respective optical activities. The near perfect asymmetric induction in the interconversion of (6) and (8) provides strong evidence against a radical pathway for racemisation of (1). Attempts to obtain some other unsymmetrically substituted 1-acylindenes foundered at the resolution stage. However 1-benzoyl-3-methoxymethyl-1-methylindene (9) was prepared from (+)-1-benzoyl-1,3-dimethylindene (see Experimental section). In the rearrangement of (9) to the isomer (10), formation of the 2-benzoylindenes (11) and (12) could not be avoided, and (9) and (10) could not be separated by chromatography on silica. Accordingly the 2*H*-indene intermediate in the rearrangement was intercepted as the *N*-phenylmaleimide adduct (13) (68% yield), $[\alpha]_D$ +6.3°, m.p. 176—178 °C; in the n.m.r. spectrum of (13) the bridgehead methyl group appeared as a singlet (τ 8.28), and this resonance was not split in the presence of tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium(III).[7] The related racemic adduct, m.p. 132—135 °C, showed two peaks (Δδ 0.3 p.p.m.) for the bridgehead methyl group in the

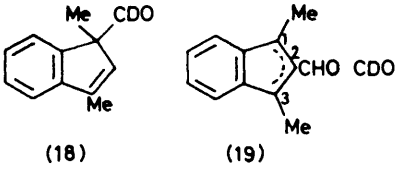


presence of the optically active shift reagent. Similarly, heating (+)-(6) with *N*-phenylmaleimide gave a mixture of the optically active adduct (14) and its 7-epimer; like (13) these showed only small optical rotations; $[\alpha]_D$ −10.3 and +15.9°, respectively. Thus, in both formyl and benzoyl migration the migrating group remains on one face of the indene molecule.

Since the rate of trapping 2*H*-indene intermediates like (3) was a poor indicator of the rate of formation of 2*H*-indenes we sought to prepare the optically active deuterium-labelled dialdehyde (15).* For (15), form-



ation of the symmetric 2*H*-indene (16) would be signalled both by loss of optical activity *and* appearance of (±)-(17) in which CHO and CDO groups have exchanged positions. Since for (16) only the reverse CHO shifts give the exchanged product (17), whilst both CHO and CDO shifts give racemic products, the rate constant for racemisation (k_{rac}) should be twice that (k_{exch}) for initial formation of (±)-(17).† This argument assumes that the secondary deuterium isotope effect for formyl migration is very small. This was confirmed for (18)



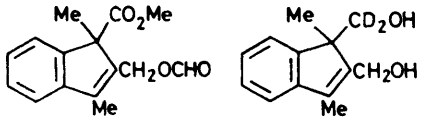
which showed $k_{rac} = 15.55 \pm 0.02 \times 10^{-5}$ s^{-1} (70 °C, decalin solvent). Under identical conditions (1) showed $k_{rac} = 15.15 \pm 0.03 \times 10^{-5}$ s^{-1}. If rearrangement of

* See note on p. 1273.

† More simply, racemisation of (16) is guaranteed but CDO–CHO exchange has a 50% probability.

(−)-(15) occurred in part by 1,3-shift (which does not allow CDO–CHO exchange) k_{rac} would be greater than 2 k_{exch}. Similarly, if racemisation occurred in part *via* a radical pair (19), $k_{rac} > 2\ k_{exch}$, as recombination of the radicals at C-3, offering no opportunity for exchange, is more likely than recombination at C-2 (see above).

The required dialdehyde (15) was prepared *via* reaction of the ester (+)-(17) with formaldehyde–formic acid (Sutherland's modification of the Prins



(20) (21)

reaction [8]) to give the formate (20). Reduction of (20) with lithium aluminium deuteride gave the diol (21) which on oxidation, first with manganese dioxide, and then with CrO_3·2Py gave (−)-(15).

Samples of (−)-(15) were heated in degassed diglyme at 120 °C and racemisation followed to *ca.* 40% and CDO–CHO exchange to *ca.* 20%. First-order plots (for 5-points) derived from polarimetric and n.m.r. measurements * on chromatographically purified mixtures of (15) and (17) gave a racemisation rate constant (k_{rac}) of $5.46 \pm 0.26 \times 10^{-5}$ s^{-1} and a rate constant for the initial conversion of (15) into (17) (k_{exch}) of $2.82 \pm 0.05 \times 10^{-5}$ s^{-1}. The k_{rac}/k_{exch} value of 1.94 ± 0.13 rules out an important racemisation route other than 2*H*-indene formation, and together with the observed asymmetric induction provides convincing evidence that the extremely easy racemisation of (1) proceeds solely by 1,5-sigmatropic formyl migration to the isoindene (3).

Racemisation of (−)-(15) is *ca.* 150 times slower than racemisation of (+)-(1).[1] This difference may reflect loss of conjugation between the indene moiety and the CHO group in the transition state of the rearrangement. Since HOMO-indene–LUMO-migrating formyl group interaction is believed to be an important feature of these reactions [1] the expected lower HOMO energy of (15) compared to (1) may also be involved. Steric factors are less likely to be important as substitution of a methyl group at C-2 in (1) accelerates rearrangement by by a factor of 1.36 at 80 °C.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. Unless otherwise specified, i.r. spectra refer to films, and n.m.r. spectra 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. Petroleum refers to light petroleum (b.p. 60—80 °C) and chromatography on silica to short-column chromatography [9] over Kieselgel G (Merck). Optical rotations were obtained using a Perkin-Elmer 141 or Thorn type 243 polarimeter. Kinetic measurements were made as previously described [1].

(+)-1-*Benzoyl*-3-*bromomethyl*-1-*methylindene*.— (+)-1-Benzoyl-1,3-dimethylindene [1,2] (350 mg, 1.41 mmol) and *N*-bromosuccinimide (303 mg, 1.7 mmol) were boiled under reflux in dry carbon tetrachloride (20 ml) containing a few crystals of benzoyl peroxide (5 h). The product was cooled in ice, filtered, and the filtrate evaporated under reduced pressure. The crude product (549 mg) was chromatographed on silica (20 g); elution with benzene–petroleum (7 : 3) gave a thick orange *oil* (470 mg, 100%) (Found: M^+, 326.030 5 and 328.029 0. $C_{18}H_{15}BrO^{79}$ and $C_{18}H_{15}BrO^{81}$ require M, 326.030 7 and 328.028 7, respectively); $\nu_{max.}$ 1 677 and 1 598 cm^{-1}; τ(60 MHz) 2.2—3.0 (9 H, m, aromatic), 3.39 (1 H, m, olefinic), 5.51 (2 H, m), and 8.42 (3 H, s); $[\alpha]_D^{24}$ +91.1° (*c* 1.063, $CHCl_3$).

(+)-1-*Benzoyl*-3-*methoxymethyl*-1-*methylindene* (+)-(9).— (+)-1-Benzoyl-3-bromomethyl-1-methylindene (208 mg, 0.636 mmol) and calcium carbonate (450 mg, 4.5 mmol) in dry methanol (10 ml) were boiled under reflux (25 h). The product was filtered, the filtrate evaporated, and the crude product (191 mg) chromatographed on silica; elution with benzene gave an *oil* (121 mg, 69%) (Found: M^+, 278.130 9. $C_{19}H_{18}O_2$ requires M, 278.130 7), $\nu_{max.}$ 1 675 and 1 598 cm^{-1}, τ(60 MHz) 2.75 (9 H, m, aromatic), 3.52 (1 H, m, olefinic), 5.51 (2 H, m), 6.63 (3 H, s), and 8.40 (3 H, s); $[\alpha]_D^{24}$ +180.5° (*c* 1.54, $CHCl_3$).

Thermolysis of (+)-1-*Benzoyl*-3-*methoxymethyl*-1-*methylindene* (+)-(9).—The title compound (264 mg) in diphenyl ether (5 ml) was heated at 145 °C under nitrogen (3.5 h). The product was chromatographed on silica (30 g); elution with benzene gave the diphenyl ether, and elution with ether–benzene (3 : 7) gave a mixture (248 mg). The latter was chromatographed on silica (42 g); elution with ether–benzene (1 : 99) gave four major fractions. Fraction 1 (61 mg) consisted of the title compound and 1-benzoyl-1-methoxymethyl-3-methylindene (10), τ (60 MHz) 2.72 (9 H, m, aromatic), 3.54 (1 H, m, olefinic), 5.84 (1 H, d, *J* 8 Hz), 6.63 (3 H, s), 6.66 (1 H, d, *J* 8 Hz), and 7.80 (3 H, d, *J* 1.5 Hz). Fraction 2 (64 mg) consisted of the title compound, 1-benzoyl-1-methoxymethyl-2-methylindene, and 2-benzoyl-3-methoxymethyl-1-methylindene (11). Fraction 3 (37 mg) was pure 2-*benzoyl*-3-*methoxymethyl*-1-*methylindene* (11) as a pale yellow oil (Found: M^+, 278.130 7. $C_{19}H_{18}O_2$ requires M, 278.130 7), $\nu_{max.}$ 1 640, 1 598, and 1 578 cm^{-1}, τ(60 MHz) 2.00—2.90 (9 H, m, aromatic), 5.71 (2 H, 2 lines of AB-system), 5.89 (1 H, q, *J* 8 and *ca.* 1 Hz), 6.80 (3 H, s), 8.68 (3 H, d, *J* 8 Hz). Fraction-4 (32 mg) consisted of 2-*benzoyl*-1-*methoxymethyl*-3-*methylindene* (12) (Found: M^+, 278.130 7), $\nu_{max.}$ 1 635, 1 598, and 1 578 cm^{-1}, τ(60 MHz) 2.02—2.77 (9 H, m, aromatic), 5.69 (1 H, m), 6.28 (1 H, dd, *J* 16 and 10 Hz), 6.36 (1 H, dd, *J* 16 and 10 Hz), 6.76 (3 H, s), and 7.95 (3 H, d, *J* 2 Hz).

Thermolysis of (+)-1-*Benzoyl*-3-*methoxymethyl*-1-*methylindene* (+)-(9) *in the Presence of* N-*Phenylmaleimide*.—The title compound (95 mg, 0.342 mmol), *N*-phenylmaleimide (237 mg, 1.37 mmol), diphenyl ether (1.5 ml), and xylene (3 ml) were boiled under reflux under nitrogen (48.5 h). The product was evaporated under reduced pressure and the residue chromatographed on silica (30 g) in ether–benzene (1 : 9) to give the endo-anti-*adduct* (13) (104 mg, 68%) as a glass. This was crystallised from methanol to give needles (71 mg), m.p. 176—178 °C (Found: M^+, 451.178 3. $C_{29}H_{25}NO_4$ requires M, 451.178 3), $\nu_{max.}$ (Nujol) 1 770, 1 707,

* The formyl protons in (15) and (17) have, as expected, very different τ-values (−0.26 and 1.19 p.p.m. respectively).

1 675, and 1 598 cm^{-1}, τ(60 MHz) 2.14 (2 H, m, aromatic), 2.40—3.10 (10 H, m, aromatic), 3.54 (2 H, m, aromatic), 5.67 (1 H, d, *J* 10 Hz), 5.84 (1 H, s), 6.06 (1 H, d, *J* 8 Hz), 6.13 (1 H, d, *J* 10 Hz), 6.60 (1 H, d, *J* 8 Hz), 6.76 (3 H, s), and 8.28 (3 H, s); $[\alpha]_D^{24}$ +6.3° (*c* 3.70, $CHCl_3$). This adduct was substantially optically pure, the resonance at τ 8.28 being unsplit in the presence of tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium(III) [7] (Eu-Optishift I). Under the same conditions the adduct, m.p. 132—135 °C (from methanol), prepared from racemic 1-benzoyl-1,3-dimethylindene showed two peaks (Δδ 0.3 p.p.m.) for this signal. An accurate assessment of the optical purity of the optically active material was prevented by the presence of a resonance due to the shift reagent in this region.

(+)-3-*Bromomethyl*-1-*methoxycarbonyl*-1-*methylindene*.—(+)-1-Methoxycarbonyl-1,3-dimethylindene [1,2] (750 mg, 3.72 mmol), *N*-bromosuccinimide (875 mg, 4.9 mmol), carbon tetrachloride (35 ml), and a few crystals of benzoyl peroxide were boiled under reflux (21.5 h). After cooling in ice the product was filtered and the filtrate evaporated under reduced pressure to give the crude title compound (1.126 g), τ(60 MHz) 2.30—2.90 (4 H, m, aromatic), 3.47 (1 H, m, olefinic), 5.63 (2 H, m), 6.45 (3 H, s), and 8.45 (3 H, s).

(+)-1-*Methoxycarbonyl*-3-*methoxymethyl*-1-*methylindene*.—The foregoing crude bromide (1.126 g), calcium carbonate (4.0 g), and pure dry methanol (80 ml) were boiled under reflux (28 h). The product was filtered, the filtrate evaporated, and the residue (1.41 g) chromatographed on silica (110 g); elution with benzene–ether (97 : 3) gave an *oil* (388 mg, 45%) (Found: M^+, 232.109 6. $C_{14}H_{16}O_3$ requires *M*, 232.109 9), $\nu_{max.}$ 1 730 cm^{-1}; τ(60 MHz) 2.40—2.97 (4 H, m, aromatic), 3.63 (1 H, t, *J* *ca.* 1 Hz), 5.61 (2 H, two strong lines of AB-system), 6.50 (3 H, s), 6.65 (3 H, s), and 8.42 (3 H, s); H_D^{24} +53.8° (*c* 1.416, $CHCl_3$).

(+)-1-*Hydroxymethyl*-3-*methoxymethyl*-1-*methylindene*.—The foregoing ester (390 mg, 1.68 mmol) in ether (40 ml) was stirred at −19 ± 2 °C under nitrogen, and lithium aluminium hydride (245 mg, 6.45 mmol) added over 5 min in three portions. The mixture was stirred at −19 °C (1 h), an excess of ethyl acetate was added, and the mixture allowed to warm to 20 °C. The product was washed with dilute sulphuric acid, washed with water, dried ($MgSO_4$), and evaporated under reduced pressure. The crude product (301 mg) was chromatographed on silica (30 g) in benzene–ether (3 : 2) to give an *oil* (250 mg, 73%) (Found: M^+, 204.114 7. $C_{13}H_{16}O_2$ requires *M*, 204.115 0), $\nu_{max.}$ 3 700—3 100 cm^{-1}, τ(60 MHz) 2.65 (4 H, m, aromatic), 3.65 (1 H, t, *J* *ca.* 1 Hz), 5.53 (2 H, two strong lines of AB-system), 6.30 (2 H, s), 6.55 (3 H, s), 8.32br (1 H, s, OH), and 8.64 (3 H, s); $[\alpha]_D^{24}$ +41.5° (*c* 1.015, $CHCl_3$).

(+)-1-*Formyl*-3-*methoxymethyl*-1-*methylindene* (+)-(6).—Chromium trioxide (1.6 g, 16 mmol) and pyridine (2.53 g, 32 mmol) were stirred in pure, dry methylene chloride (40 ml) under nitrogen (15 min) before addition of (+)-1-hydroxymethyl-3-methoxymethyl-1-methylindene (229 mg, 1.12 mmol) in methylene chloride (5 ml). After stirring for 15 min, ether was added and the ether layer washed with aqueous sodium hydroxide, dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water, dried ($MgSO_4$), and evaporated. The crude product (182 mg) was chromatographed on silica (30 g); elution with benzene–ether (97 : 3) gave an *oil* (151 mg, 67%) (Found: M^+, 202.099 6. $C_{13}H_{14}O_2$ requires *M*, 202.099 4), $\nu_{max.}$ 1 720 cm^{-1}, τ(60 MHz) 1.50 (1 H, s, CHO), 2.68 (4 H, m, aromatic), 3.84 (1 H, t, *J* *ca.* 1 Hz), 5.48 (2 H, two strong lines of AB-system), 6.54 (3 H, s), and 8.50 (3 H, s); $[\alpha]_D^{24}$ +125.1° (*c* 1.20, $CHCl_3$).

Thermolysis of (+)-1-*Formyl*-3-*methoxymethyl*-1-*methylindene*.(+)-(6).—The title compound (140 mg) and dry benzene (10 ml) were refluxed under nitrogen (3 h). Evaporation of solvent under reduced pressure at 20 °C gave the crude product which was chromatographed on silica (30 g); elution with ether–benzene (1 : 49) gave (−)-1-*formyl*-1-*methoxymethyl*-3-*methylindene* (−)-(8) (94 mg) as an oil (Found: M^+, 202.099 8. $C_{13}H_{14}O_2$ requires *M*, 202.099 4), $\nu_{max.}$ 1 722 cm^{-1}, τ(60 MHz) 1.18 (1 H, s, CHO), 2.60 (4 H, m, aromatic), 3.84 (1 H, q, *J* *ca.* 1.5 Hz), 6.02 (1 H, d, *J* 9 Hz), 6.29 (1 H, d, *J* 9 Hz), 6.62 (3 H, s), and 7.76 (3 H, d, *J* *ca.* 1.5 Hz); $[\alpha]_D^{24}$ −65.7° (*c* 1.283, $CHCl_3$). Further elution gave recovered starting material (41 mg), $[\alpha]_D^{24}$ +123.7° (*c* 1.093, $CHCl_3$). The initial rate constant for the isomerisation of (+)-(6) to (−)-(8) was estimated (n.m.r.) to be 47 × 10^{-5} at 80 °C in benzene, giving a half-life of *ca.* 25 min.

Thermolysis of (−)-1-*Formyl*-1-*methoxymethyl*-3-*methylindene* (−)-(8).—The title compound [95 mg, $[\alpha]_D^{24}$ −65.7° (*c* 1.283, $CHCl_3$)] in dry benzene (10 ml) was refluxed under nitrogen (3.5 h). Chromatography of the product on silica (30 g) in benzene–ether (49 : 1) gave (−)-1-formyl-1-methoxymethyl-3-methylindene(−)-(8) (57 mg), $[\alpha]_D^{24}$ −65.1° (*c* 1.166, $CHCl_3$), and (+)-1-formyl-3-methoxymethyl-1-methylindene(+)-(6) (27 mg), $[\alpha]_D^{24}$ +122.9° (*c* 0.624, $CHCl_3$).

When a mixture of (+)-(6) (25 mg) and (−)-(8) (45 mg) was thermolysed as above (48 h) chromatographic isolation as described previously gave (+)-1-formyl-3-methoxymethyl-1-methylindene (+)-(6) (18 mg), $[\alpha]_D^{24}$ +119° ($CHCl_3$), and (−)-1-formyl-1-methoxymethyl-3-methylindene (−)-(8) (47 mg), $[\alpha]_D^{24}$ −63.5° ($CHCl_3$).

Thermolysis in the Presence of N-*Phenylmaleimide*.—A mixture (40 mg, 0.2 mmol) of (+)-1-formyl-3-methoxymethyl-1-methylindene (+)-(6) (2 parts), (−)-1-formyl-1-methoxymethyl-3-methylindene (−)-(8) (1 part), *N*-phenylmaleimide (140 mg, 0.8 mmol), and diphenyl ether (2 ml) were heated at 120 °C under nitrogen (46 h). The mixture was chromatographed on silica (30 g); elution with benzene–ether (9 : 1) gave first diphenyl ether and *N*-phenylmaleimide, and then the syn-endo-*adduct* [7-epimer of (14)] (13 mg, 17%) as a glass (Found: M^+, 375.147 4. $C_{23}H_{21}NO_4$ requires *M*, 375.147 0), $\nu_{max.}$ 1 775, 1 710, and 1 598 cm^{-1}, τ(60 MHz) 0.04 (1 H, d, *J* 2.5 Hz), 2.5—3.0 (7 H, m, aromatic), 3.4—3.7 (2 H, m, aromatic), 5.60 (1 H, d, *J* 10 Hz), 5.80 (1 H, d, *J* 10 Hz), 6.10 (1 H, d, *J* 8 Hz), 6.21 (1 H, d, *J* 8 Hz), 6.46 (3 H, s), 7.02 (1 H, d, *J* 2.5 Hz), and 8.13 (3 H, s); $[\alpha]_D^{24}$ +15.9° (*c* 1.341, $CHCl_3$).

Continued elution of the column gave the anti-endo-*adduct* (14) (44 mg, 59%) as a glass (Found: M^+, 375.147 4), $\nu_{max.}$ 1 775, 1 710, and 1 598 cm^{-1}; τ(60 MHz) 0.83 (1 H, d, *J* 4 Hz), 2.4—3.0 (7 H, m, aromatic), 3.35—3.65 (2 H, m, aromatic), 5.68 (1 H, d, *J* 10 Hz), 5.80 (1 H, d, *J* 10 Hz), 6.31 (1 H, d, *J* 8.5 Hz), 6.50 (3 H, s), 6.59 (1 H, d, *J* 8.5 Hz), 7.10 (1 H, d, *J* 4 Hz), and 8.15 (3 H, s); $[\alpha]_D^{24}$ −10.3° (*c* 2.107, $CHCl_3$). Neither these adducts nor the derived oximes could be obtained in crystalline form. The adducts were prepared in racemic form and their n.m.r. spectra determined in the presence of Eu-Optishift I (see above); no significant splitting of the above signals was observed.

(+)-1-*Deuterioformyl*-1,3-*dimethylindene* (+)-(18).—(+)-1,3-Dimethylindene-1-carboxylic acid (700 mg, 3.72 mmol) was treated with lithium aluminium deuteride (244 mg, 5.8 mmol) in ether (20 ml) with stirring at −20 °C under nitrogen. After 1 h the mixture was allowed to reach 20 °C over 30 min. Addition of water and separation, drying ($MgSO_4$), and evaporation of the ether layer gave the crude alcohol (627 mg). Oxidation of the alcohol (627 mg) with CrO_3·2Py over 1 h and work-up as described above for the preparation of (+)-(6) gave a crude product (464 mg) which was purified by silica chromatography in benzene to give (+)-(18) as an *oil* (148 mg, 23%) (Found: M^+, 173.095 2. $C_{12}H_{11}DO$ requires M, 173.095 1), $\nu_{max.}$ 2 110, 2 055, 1 708, and 1 677 cm^{-1}; τ(60 MHz) 2.5—2.8 (4 H, m, aromatic), 4.10 (1 H, q, J 1.5 Hz), 7.78 (3 H, d, J 1.5 Hz), and 8.53 (3 H, s); $[\alpha]_D^{24}$ +130.8° (*c* 1.10, $CHCl_3$).

(+)-2-*Formyloxymethyl*-1-*methoxycarbonyl*-1,3-*dimethylindene* (+)-(20).—Paraformaldehyde (1.4 g) and 98% formic acid (10 ml) were boiled under reflux to effect solution, the mixture cooled to 20 °C and paraformaldehyde (1 g) added followed by (+)-1-methoxycarbonyl-1,3-dimethylindene (500 mg, 2.48 mmol) in formic acid (1 ml).[8] After stirring (19 h) the product was diluted with water, and extracted with ether. The ether layer was washed with water, sodium hydrogen carbonate solution, and water, dried ($MgSO_4$), and evaporated to give a crude product (570 mg) which was chromatographed on silica in ether–benzene (1 : 9) to give the impure title compound (260 mg) (*ca.* 40% impurity). The racemic title compound was prepared in the same way and purified by crystallisation from petroleum to give (±)-2-*formyloxy*-1-*methoxycarbonyl*-1,3-*dimethylindene* (±)-(20) as needles m.p. 77—80° (Found: C, 69.35; H, 6.1. $C_{15}H_{16}O_4$ requires C, 69.2; H, 6.2%), $\nu_{max.}$ 1 725 and 1 730 cm^{-1}, τ(60 MHz) 1.92br (1 H, s, CHO), 2.68 (4 H, m, aromatic), 4.89 (2 H, s), 6.43 (3 H, s), 7.81 (3 H, s), and 8.41 (3 H, s).

(+)-1-*Hydroxydideuteriomethyl*-2-*hydroxymethyl*-1,3-*dimethylindene* (+)-(21).—(+)-2-Formyloxymethyl-1-methoxycarbonyl-1,3-dimethylindene (+)-(20) (1.98 g, *ca.* 80% pure by n.m.r.) in ether (125 ml) was stirred under nitrogen at −20 °C, and lithium aluminium deuteride (1.6 g, 38 mmol) was added over 5 min in three portions. The mixture was stirred at −20 °C for 1 h and allowed to reach room temperature over 30 min. After addition of water the ether layer was separated, washed with water, dried ($MgSO_4$), evaporated, and the crude product (1.55 g) chromatographed on silica (130 g); elution with ethyl acetate–benzene (1 : 1) gave an *oil* (1.09 g) (Found: M^+, 206.128 6. $C_{13}H_{14}D_2O_2$ requires M, 206.127 6), $\nu_{max.}$ 3 700—2 600, 2 200, 2 085, and 1 650 cm^{-1}; τ(60 MHz) 2.74 (4 H, m, aromatic), 5.08br (2 H, s, OH), 5.44 (1 H, d, J 12 Hz), 5.82 (1 H, d, J 12 Hz), 7.93 (3 H, s), and 8.70 (3 H, s); $[\alpha]_D^{24}$ +139° (*c* 1.115, $CHCl_3$).

(+)-2-*Formyl*-1-*hydroxydideuteriomethyl*-1,3-*dimethylindene*.—The foregoing diol (1.09 g, 5.32 mmol), manganese dioxide (1.8 g, activated) in benzene (30 ml) and petroleum (130 ml) were stirred at 20 °C. Further portions (1 g) of the oxidant were added after 13.5 and 16 h, and after 17.5 h the mixture was filtered, and the filtrate evaporated to give the title compound as an *oil* (985 mg, 90%) (Found: M^+, 204.112 8. $C_{13}H_{12}D_2O_2$ requires M, 204.111 9), $\nu_{max.}$ 3 420, 2 200, 2 090, 1 650br, and 1 580 cm^{-1}; $\lambda_{max.}$ (EtOH) 234 and 307 nm (ε 6 200 and 11 300); τ(60 MHz) −0.12 (1 H, s, CHO), 2.3—2.9 (4 H, m, aromatic), 6.15br (1 H, s, OH), 7.51 (3 H, s), and 8.59 (3 H, s); $[\alpha]_D^{24}$ +104° (*c* 2.235, $CHCl_3$).

(−)-1-*Deuterioformyl*-2-*formyl*-1,3-*dimethylindene* (−)-(15).—Chromium trioxide (2.9 g, 29 mmol) and pyridine (4.59 g, 58 mmol) were stirred in methylene chloride (100 ml) under nitrogen (15 min) before addition of (+)-2-formyl-1-hydroxydideuteriomethyl-1,3-dimethylindene (985 mg, 4.83 mmol) in methylene chloride (5 ml). After stirring (40 min) the mixture was diluted with ether, and the solution washed with saturated aqueous sodium hydrogen carbonate, washed with dilute hydrochloric acid containing sodium chloride and saturated aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated. The crude product (896 mg) was chromatographed on silica (120 g); elution with ether–benzene (1 : 9) gave (−)-(15) as needles (539 mg, 55%), m.p. 75—77° (from benzene–petroleum) (Found: C, 77.9; H, 6.3. $C_{13}H_{11}DO_2$ requires C, 77.6; H + D, 6.5%), $\nu_{max.}$ (Nujol) 2 120, 2 065, 1 715, 1 650, and 1 600 cm^{-1}; $\lambda_{max.}$ (EtOH) 236 and 307.5 nm (ε 7 870 and 15 350), τ(60 MHz) −0.26 (1 H, s, CHO), 2.2—2.8 (4 H, m, aromatic), 7.37 (3 H, s), and 8.39 (3 H, s); $[\alpha]_D^{24}$ −43.0° (*c* 1.010, C_6H_6).

Thermolysis of (−)-1-*Deuterioformyl*-2-*formyl*-1,3-*dimethylindene* (−)-(15).—The title compound (87 mg) in pure diglyme (0.5 ml) was degassed (4 freeze–thaw cycles) and sealed in an n.m.r. tube. This was heated at 120 °C (2.5 h), and the crude product (87 mg) chromatographed on silica (25 g); elution with benzene–ether (9 : 1) gave a mixture of the title compound and (−)-2-deuterioformyl-1-formyl-1,3-dimethylindene which was analysed by n.m.r. (90 MHz) (showing 21.4% exchange had occurred) and polarimetry (showing a loss of 39.6% in optical activity). Fresh samples were analysed in the same way after heating for 1.0, 1.5, and 2.0 h.

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