1,5-Sigmatropic Formyl Migration in 1,3-Dimethylbenz[*f*]indene-1-carbaldehyde; Evidence for Product-like Transition States

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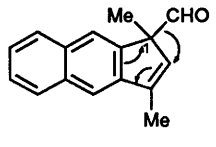
The title compound **1** has been prepared in an optically active form *via* a convenient seven-step sequence. The migratory ability of the formyl group allows the 1,5-shift **1** (arrows) involving disruption of naphthalene aromaticity to proceed with modest activation [$\Delta G^{\ddagger}$ = 31.84 ± 0.6 kcal mol^{-1} (145 °C)]. Activation enthalpies for 1,5-formyl migration in **1**, **3**, **4** and **5** correlate well with changes in π-electron energy in going from these compounds to their respective rearrangement products. Product-like transition states involving important cleavage of the bond between the migration origin and the formyl group are suggested for these rearrangements.

Replacement of a double bond involved in a pericyclic reaction by a benzene ring has a modest and variable effect on the activation enthalpy (1–12 kcal mol^{-1}).[1] This has been attributed[1a] to the aromatic character of the pericyclic transition state (TS). If a non-annelated reactant goes to a TS resembling benzene the benzannelated one goes to a TS resembling naphthalene. In the latter case benzene delocalisation in the ground state is not destroyed but replaced by naphthalene-type delocalisation at the TS. To further explore this effect we have prepared the optically active benz[*f*]indene **1** and compared its 1,5-sigmatropy **1** ⟶ **2** with that previously studied in compounds **3**,[2a] **4**,[2c] and **5**.[2b] It was expected that this would provide a more comprehensive study of the effect of benzannelation upon pericyclic TS's than hitherto available and would allow us to test quantitative correlation of activation enthalpy with loss of π-electron energy in going to the 2*H*-indene intermediates. Information about the TS in 1,5-formyl migration was also expected to accrue.

Preparation of 1,3-*Dimethylbenz*[f]*indene*-1-*carbaldehyde*.—1,3-Dimethylbenz[*f*]indene **6** required for the synthesis of **1** was obtained in two ways. The commercially available but expensive naphthalene-2,3-dicarboxylic acid could be converted *via* benz[*f*]indan-1,3-dione into the oxime **7** as previously described.[3] Reaction of **7** with methylmagnesium iodide gave the diol **8**. Reduction of **8** with HI–HOAc gave an unstable ketone **9** which could be utilised by immediate reduction ($LiAlH_4$) to a mixture of alcohols which were dehydrated to **6** (PPh_3, CBr_4). A more efficient route to **6** started by reaction of the tetrabromide **10** with sodium iodide in the presence of the cyclopentenone **11**. The transient *o*-quinodimethane **12** is trapped by **11** to give **13**. Under the reaction conditions this spontaneously loses two molecules of HBr to give **14** in 35% yield. Reaction of **14** with MeMgI and acid-catalysed dehydration during work-up gave **6** in 68% yield. The acid **15** was available in 89% yield by reaction of the lithium salt of **6** with solid CO_2. Attempts to resolve **15** using quinine, brucine and α-phenylethylamine met with no success, and the diastereoisomeric menthyl esters of **15** could not be resolved by chromatography or crystallisation. Finally it was found that the diastereoisomeric (*S*)-(−)-α-methylbenzyl esters **16**, prepared from **15** and (*S*)-(−)-α-methylbenzyl alcohol in the presence of dicyclohexylcarbodi-imide, 4-dimethylaminopyridine (DMAP), and DMAP·HCl,[4] deposited only one diastereoisomer from ether–hexane. This diastereoisomer was converted into the

Table 1. Changes in resonance energy and activation enthalpies for [1,5] formyl migration.

		Hückel		Dewarpi		
	$\Delta H^{\ddagger}$	$\Delta E\pi$	$\Delta E_{biradical}$	$\Delta E\pi$	$\Delta E\pi$	$\Delta E_{biradical}$
Compd.	kcal mol^{-1}	β	β	eV	kcal mol^{-1}	eV
4	13.2	0.000	1.644	0.000	0.000	2.203
5	16.0	0.215	1.632	0.250	5.760	2.399
3	22.08	0.470	1.703	0.733	16.888	2.403
1	27.38	0.579	1.684	1.078	24.837	2.428



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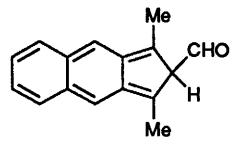

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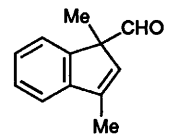

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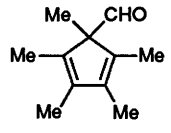

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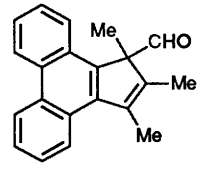

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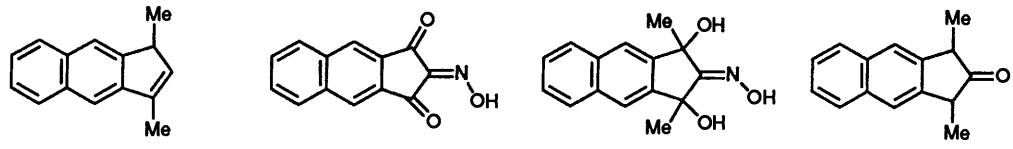

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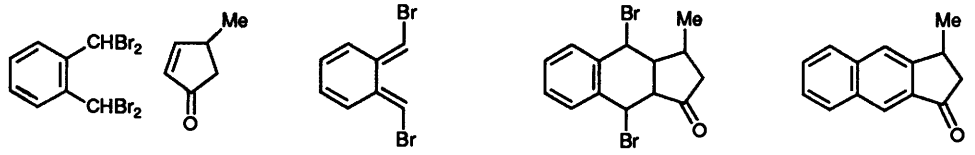

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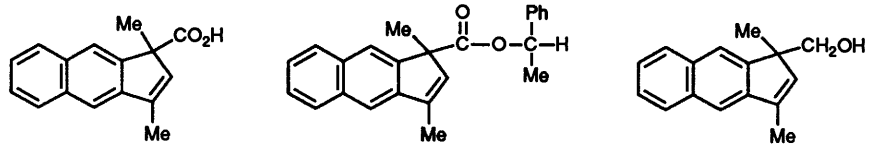
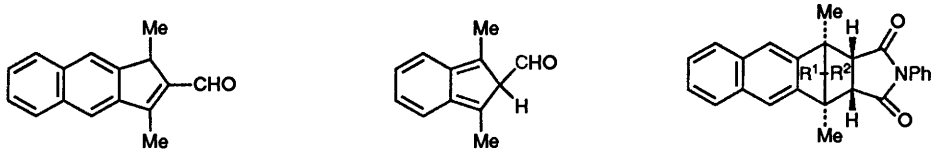


15 16 17

optically active alcohol **17** by reduction ($LiAlH_4$, 89%). Swern oxidation of **17** gave **1** in 89% yield, $[\alpha]_D^{25} = -214°$ (*c*, 1.91, $CHCl_3$).

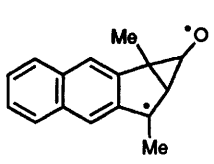
Thermolysis of 1,3-*Dimethylbenz*[f]*indene*-1-*carbaldehyde*.—The racemic aldehyde **1** was heated in degassed deuteriobenzene in a sealed tube which fitted snugly inside an ordinary NMR tube. ^1H NMR monitoring of the thermolysis showed that after 87 min at 230 °C, 64.4% of **1** remained unchanged and only 3.4% of the indene-2-carbaldehyde **18** was observed. The main thermolysis product was the indene **6** produced by decarbonylation. This behaviour contrasts with that of 1,3-dimethylindene-1-carbaldehyde which gives mainly 1,3-dimethylindene-2-carbaldehyde and little if any decarbonylation product. A more ready homolysis of the C(1)–CHO bond in naphthalene **1** than in the benzene derivative **3** may explain these results. A second factor may be the lower stationary concentration of the 2*H*-indene **2** from **1** than of the related 2*H*-indene **19** from **3**. The 2*H*-indene intermediate would be expected to form more slowly and to revert to the indene more rapidly in the naphthalene compounds. This is consistent with the slower trapping of **2** than of **19** with *N*-phenylmaleimide. Thus the *syn* and *anti* adducts **20** and **21** of **2** are formed in 68% yield after heating **1** at 160 °C with 20 equiv. of *N*-phenylmaleimide over 112 h. The related adducts from **19** were obtained in 78% yield after heating **3** at 80 °C with 3 equiv. of *N*-phenylmaleimide for 70 h.

When heated at 130 °C in diphenyl ether **1** underwent racemisation without significant formation of other products. Loss of optical activity followed good first-order kinetics and gave the following rate constants [$10^5 k/s^{-1}$ (T/°C)]: 5.50 (130), 12.79 (140), 30.09 (150), 62.16 (160); and the activation parameters, $\Delta H^{\ddagger} = 27.38 \pm 0.42$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -10.68 \pm 1.0$ cal K^{-1} mol^{-1}. The activation entropy is very similar to that for the racemisation of **3** (-11.41 ± 2.21 cal K^{-1} mol^{-1}) and supports racemisation *via* a concerted formyl migration to the isoindene **2**. Activation enthalpies ($\Delta H^{\ddagger}$) for 1,5-formyl migration in compounds **1**, **3**, **4** and **5** are collected in Table 1 together with the decreases in π-electron energy ($\Delta E\pi$) accompanying rearrangement. For the rearrangement of **3** to **19**, $\Delta E\pi$ is the difference in π-electron energy between styrene and *o*-quinodimethane. Values of $\Delta E\pi$ derived from π-electron energies determined by both Hückel and Dewar-π calculations [5] are given in Table 1. The correlation of $\Delta H^{\ddagger}$ with $\Delta E\pi$ (Hückel) is fair (correlation coefficient 0.973) but the correlation of $\Delta H^{\ddagger}$ with $\Delta E\pi$ (Dewar-π) is better (correlation coefficient 0.998) (Fig. 1). These correlations are consistent with product like TS's for the rearrangement of **1**, **3** and **5**. This agrees with Hammond's postulate. The TS's should resemble the reactive intermediates *e.g.* **2** and **19**. This conclusion implies important cleavage of the 'old bond,' *i.e.* the C(1)–CHO bond in **1** and **3** in going to the TS's. This is at variance with the view [6] that easier migration of unsaturated compared with saturated groups can be explained if the 'major process occurring on the way to the TS is formation of the new σ-bond at the expense of the relatively weak π-bonds, the old σ-bond being almost unbroken.' This view would suggest that the TS's for rearrangement of **1**, **3**, **4** and **5** resemble the respective biradicals **22**, **23**, **24** and **25**.[6] The change in π-energy in going from **1**, **3**, **4** and **5** to the biradicals ($\Delta E_{biradical}$) was calculated *e.g.* for **3** going to **23** as the difference in π-energy between styrene and a benzyl radical. The energy changes ($\Delta E_{biradical}$) calculated by both the Hückel and Dewar-π methods are given in Table 1; the correlation of this data with



18 19

20; R^1 = CHO, R^2 = H
21; R^1 = H, R^2 = CHO



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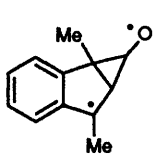

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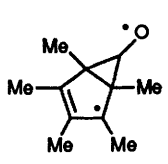

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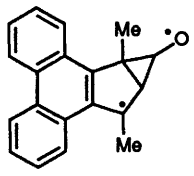

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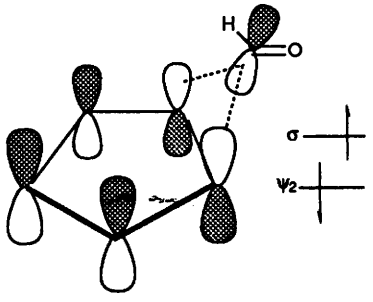

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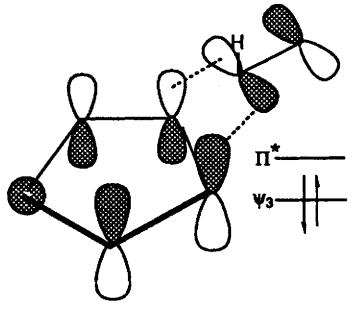

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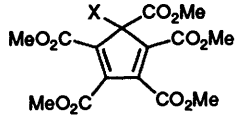

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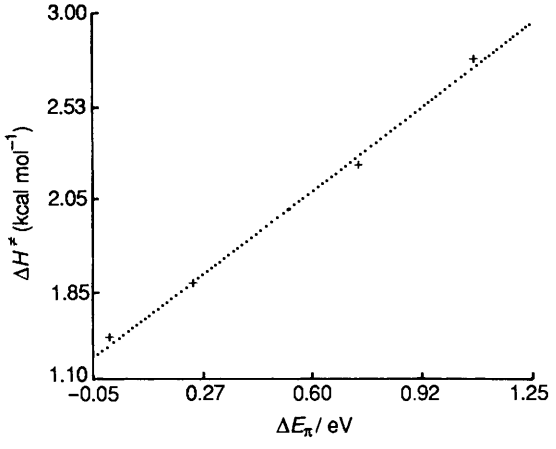

Fig. 1. Plot of $\Delta H^{\ddagger}$ (kcal mol^{-1}) against $\Delta E\pi$ (eV) from Dewarpi SCF-MO calculations. Scale: *Y* values = *Y**E1 and *X* values = *X**EO.

the measured activation enthalpies is very poor (correlation coefficients 0.695 and 0.757 respectively). Our results are in better agreement with the secondary interaction approach proposed earlier to explain easy formyl migration[2] and variations in the migratory aptitude of *E*-vinyl groups.[7] The TS is modelled as two strongly interacting radicals, *e.g.* a cyclopentadienyl radical and HC=O for formyl migration on a cyclopentadiene. In addition to the type of interaction considered by Woodward and Hoffmann[8] involving the singly occupied formyl and cyclopentadienyl ψ_2 orbitals (see **26**) there is an important secondary interaction between the degenerate cyclopentadienyl ψ_3 orbital and the vacant carbonyl π^*-orbital as in **27**. The interaction in **26** can account for important old bond cleavage at the TS and the interaction in **27** can explain TS stabilisation involving an unsaturated migrating group. Further evidence suggesting important cleavage of the old bond in the TS of these rearrangements comes from a study of the rate of CO_2Me migration in the cyclopentadienes **28**; **28** (X = NMe_2) rearranges *ca.* 780 times faster than **28** (X = Cl).[9a] Related effects have been observed for phenyl migration in indenes.[9b]

Experimental

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. Unless otherwise stated, IR spectra refer to Nujol mulls, UV spectra to ethanol solutions, and ^{1}H NMR spectra to solutions in deuteriochloroform measured at 90 MHz with a Perkin-Elmer R32 or a JEOL FX90Q instrument. 400 MHz Spectra were obtained on a Bruker WH-400 instrument. Low resolution mass spectra were obtained with a Kratos MS25 instrument and accurate mass measurements were made using a Kratos MS9150 instrument. Where accurate mass measurement was used to establish molecular formulae the purity of the sample was checked by TLC in more than one solvent system as well as by NMR measurements, and for crystalline material by crystallisation to constant m.p. Chromatography on silica refers to short-column chromatography[10] over Kieselgel G (Merck). Ether refers to diethyl ether and light petroleum to the fraction b.p. 60–80 °C.

1,3-*Dihydroxy*-1,3-*dimethylbenz*[f]*indan*-2-*one* 2-*Oxime* **8**.—A solution of iodomethane (5.166 g, 36 mmol) in ether (36 ml) was added to magnesium turnings (600 mg, 25 mmol) and the mixture refluxed until no magnesium remained. A portion of this solution (23.2 ml) was added to a solution of benz[*f*]indan-1,2,3-trione 2-oxime (1 g, 4 mmol) in benzene (20 ml) at 0–5 °C. After being stirred for 30 min the mixture was refluxed for 90 min. The cooled mixture was diluted with benzene and washed with saturated aqueous ammonium chloride and brine, dried ($MgSO_4$) and evaporated to give a solid (791 mg). Chromatography on silica with benzene–ethanol (95:5) gave the *title compound* **8** as a solid (332 mg, 33%); m.p. 135–136 °C (from ethanol–hexane) (Found: C, 70.3; H, 6.05; N, 5.2%; M^+, 257.105. $C_{15}H_{15}NO_3$ requires C, 70.0; H, 5.8; N, 5.4%; M, 257.105); ν_{max}/cm^{-1}(Nujol): 3300; δ_H[90 MHz; $CDCl_3$–$(CD_3)_2SO$] 10.9 (1 H, s), 7.9 (4 H, m, aromatic), 7.45 (2 H, m, aromatic), 5.00 (1 H, s), 4.80 (1 H, s), 1.90 (3 H, s) and 1.75 (3 H, s); *m*/*z* 257, 239, 224, 206, 197, 178, 165, 152, 141 and 127 (36.8, 68.5, 89.6, 54.6, 100.0, 37.0, 25.0, 35.8, 23.1 and 30.9%).

1,3-*Dimethylbenz*[f]*indene* **6**.—The 2-oxime **8** (210 mg, 0.8 mmol) was mixed with glacial acetic acid (10.5 ml), hydriodic acid (2.69 g) and red phosphorus (*ca.* 30 mg) and the mixture heated for 15 min at 100 °C. The solution was cooled, diluted

with dichloromethane, washed with 20% aqueous potassium iodide and water, dried (Na_2SO_4) and evaporated to give the title compound as an oil (157 mg). 1,3-Dimethylbenz[*f*]indan-2-one (157 mg, crude) was dissolved in tetrahydrofuran (10 ml) and the solution cooled to *ca.* −72 °C. Lithium aluminium hydride (156 mg, 4.1 mmol) was added in small portions over 5 min and the suspension stirred for 60 min before being being warmed to room temperature. Dichloromethane and 1M sulphuric acid were added and the aqueous phase was extracted with dichloromethane. The combined organic phases were washed with water, dried (Na_2SO_4) and evaporated to give an oil (183 mg). Chromatography of this on silica with hexane–ether (85:15) gave a mixture of two 1,3-dimethylbenz[*f*]indan-2-ols as an oil (78 mg, 44%). This mixture (39 mg, 0.19 mmol) and carbon tetrabromide (126 mg, 0.38 mmol) were dissolved in benzene (3 ml) and triphenylphosphine (100 mg, 0.38 mmol) was added. After 9 h carbon tetrabromide (126 mg, 0.38 mmol) and triphenylphosphine (100 mg, 0.38 mmol) were added. After 14.5 h the mixture was diluted with dichloromethane, washed with brine, dried ($MgSO_4$) and evaporated to give an oil (415 mg). Chromatography of this on silica with hexane–benzene (99:1) gave the *title compound* **6** as an oil (15.4 mg, 18%) and a mixture of the two 2-bromo-1,3-dimethylbenz[*f*]indanes (11.3 mg) as a solid. 2-Bromo-1,3-dimethylbenz[*f*]indane (11.3 mg) was dissolved in 1,8-diazabicyclo[5.4.0]undec-7-ene (1 ml) and toluene (3 ml). After 5 h the mixture was diluted with dichloromethane and 1M hydrochloric acid added. The aqueous layer was extracted with dichloromethane and the combined organic extracts were washed with 1M aqueous sodium hydrogen carbonate and brine. Drying ($MgSO_4$) and evaporation gave an oil (14 mg). Flash chromatography of this on silica with hexane–benzene (98:2) gave 1,3-dimethylbenz[*f*]indene as an oil (3.9 mg, 5%). The total yield of the indene from the indanol was therefore 23%.

3-*Methylbenz*[f]*indane*-1-*one* **14**.—α,α,α′,α′-Tetrabromo-*o*-xylene (553 mg, 1.3 mmol), sodium iodide (1.3 g, 8.7 mmol) and 4-methylcyclopent-2-enone[11] (125 mg, 1.3 mmol) were mixed in dimethylformamide (5 ml).[12] The mixture was heated at 70 °C for 23 h, cooled, diluted with dichloromethane and shaken with 20% aqueous sodium metabisulphite. The aqueous phase was extracted with dichloromethane and the combined extracts were washed with brine, dried ($MgSO_4$) and evaporated to give an oil (309 mg). Chromatography of this on silica with benzene–ether (96:4) gave the *title compound* **14** as an oil which solidified with time (90 mg, 35%), m.p. 85–86 °C (from dichloromethane–hexane) (Found: C, 85.5; H, 6.1; M^+, 196.088. $C_{14}H_{12}O$ requires: C, 85.7; H, 6.1%; M, 196.089); ν_{max}/cm^{-1}(Nujol): 1710, 1625 and 760; δ_H(90 MHz) 8.29 (1 H, s), 7.85 (3 H, m, aromatic), 7.51 (2 H, m, ArH), 3.58 (1 H, m), 3.05 (1 H, dd, *J*/Hz: 14, 6), 2.40 (1 H, dd, *J*/Hz: 14, 6) and 1.50 (3 H, d, *J*/Hz: 6); *m/z* 196, 181, 168, 152, 139, 126, 115, 84 and 76 (100.0, 78.6, 30.4, 61.4, 78, 19.2, 7.4, 7.1 and 20.5%).

1,3-*Dimethylbenz*[f]*indene* **6**.—A solution of iodomethane (1.343 g, 9.5 mmol) in ether (15 ml) was added to magnesium turnings (150 mg, 4.3 mmol) and the mixture refluxed until no magnesium remained. A portion of the Grignard solution (9 ml, 3.8 mmol) was added dropwise to a solution of 3-methylbenz[*f*]indan-1-one in ether (15 ml) at 0 °C. After 10 min the solution was warmed and refluxed for 30 min. The cooled solution was diluted with dichloromethane and rapidly shaken with 3M sulphuric acid. The aqueous layer was extracted with dichloromethane and the combined extracts were washed with brine, dried ($MgSO_4$) and evaporated to give an oil (364 mg). Flash chromatography of this on silica with hexane–benzene (98:2) gave the *title compound* **6** as an oil (255 mg, 68%) (Found: M^+, 194.110. $C_{15}H_{14}$ requires M, 194.110); ν_{max}/cm^{-1}(film): 2960, 1620, 1460, 880 and 760; δ_H(90 MHz) 7.85 (3 H, m, ArH), 7.65 (1 H, s), 7.4 (2 H, m, aromatic), 6.2 (1 H, m), 3.55 (1 H, m), 2.2 (3 H, m) and 1.35 (3 H, d, *J*/Hz: 6); *m/z* 194, 179, 165, 152 and 89 (64.2, 100.0, 11.7, 10.0 and 17.8%).

1,3-*Dimethylbenz*[f]*indene*-1-*carboxylic Acid* **15**.—Butyllithium (1.6M solution in hexane; 1.38 ml, 2.21 mmol) was added to a solution of 1,3-dimethylbenz[*f*]indene (357 mg, 1.8 mmol) in ether (20 ml) at 0 °C. After 5 min solid carbon dioxide was added, and the solution allowed to warm to room temperature. The mixture was extracted with 1M aqueous sodium hydrogen carbonate, and the combined extracts were acidified with concentrated hydrochloric acid. The mixture was extracted with ether, and the extract dried ($MgSO_4$) and evaporated to give the *title compound* **15** as a solid (391 mg, 89%), m.p. 195 °C (from ether–hexane) (Found: C, 80.7; H, 5.8; M^+, 238.099. $C_{16}H_{14}O_2$ requires C, 80.7; H, 5.9%; M, 238.099); ν_{max}/cm^{-1} (Nujol): 1690; δ_H(90 MHz) 11.2 (1 H, br s), 7.85 (3 H, m, ArH), 7.6 (1 H, s), 7.45 (2 H, m, ArH), 6.2 (1 H, q, *J*/Hz: 2), 2.2 (3 H, d, *J*/Hz: 2) and 1.6 (3 H, s); *m/z* 238, 193, 178, 165, 152, 89, 73 and 100 (31.2, 100.0, 44.9, 9.5, 6.9, 7.1, 11.0 and 29.7%).

(±)-1,3-*Dimethylbenz*[f]*indene*-1-*carbaldehyde* **1**.—A solution of 1,3-dimethylbenz[*f*]indene-1-carboxylic acid (62.7 mg, 0.26 mmol) in tetrahydrofuran (4 ml) was stirred at −74 °C for 10 min. Lithium aluminium hydride (21.1 mg, 0.56 mmol) was added in small portions, and the suspension stirred for 60 min before being warmed to room temperature. It was diluted with water, dichloromethane, and dilute sulphuric acid and the organic layer was separated. The aqueous layer was extracted with dichloromethane and the combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated to give (±)-1-hydroxymethyl-1,3-dimethylbenz[*f*]indene as an oil (49 mg). A solution of dimethyl sulphoxide (41 mg, 0.53 mmol) in dichloromethane (2 ml) was stirred at −74 °C and oxalyl chloride (32 mg, 0.25 mmol) in dichloromethane (1 ml) was added. After 5 min (±)-1-hydroxymethyl-1,3-dimethylbenz[*f*]indene (49 mg, 0.22 mmol) in dichloromethane (2 ml) was added dropwise, and the solution stirred for 15 min. Triethylamine (111 mg, 1.1 mmol) in dichloromethane (1 ml) was added dropwise and the solution stirred for 10 min before being warmed to room temperature. It was then diluted with dichloromethane and water and the aqueous phase separated and extracted with dichloromethane. The combined extracts were washed with 1M hydrochloric acid, 1M aqueous sodium hydrogen carbonate and brine, dried ($MgSO_4$) and evaporated to give an oil (40.6 mg). Chromatography of this on silica with hexane–benzene (65:35) gave the title compound **1** as an oil (17 mg, 31%).

(−)-1-*Phenylethyl* 1,3-*Dimethylbenz*[f]*indene*-1-*carboxylate* **16**.—1,3-Dimethylbenz[*f*]indene-1-carboxylic acid (100 mg, 0.42 mmol), 4-dimethylaminopyridine (5.6 mg, 0.04 mmol), 4-dimethylaminopyridine hydrochloride (7.3 mg, 0.04 mmol) and (−)-1-phenylethyl alcohol (56.4 mg, 0.43 mmol) were dissolved in dichloromethane (10 ml). Dicyclohexylcarbodiimide (95.3 mg, 0.43 mmol) was added to the mixture and the solution stirred for 18 h. The mixture was diluted with ether, filtered and then washed with 1M hydrochloric acid, 1M aqueous sodium hydrogen carbonate and brine. After being dried ($MgSO_4$) the mixture was evaporated to give an oil (138 mg) which by flash chromatography on silica with hexane–ether (90:10) provided an oil (107 mg, 74%). The mixture of diastereoisomers (434 mg) was crystallised from ether–hexane to give the *title compound* **16** (193 mg, 45%), m.p. 148–149 °C (from ether–hexane); $[\alpha]_D^{25}$ −182° (*c* 0.69, $CHCl_3$) (Found: C, 84.15; H, 6.4%; M^+, 342, 161). $C_{24}H_{22}O_2$ requires: C, 84.2; H, 6.4%; M, 342.162); ν_{max}/cm^{-1}(Nujol): 1710; δ_H(90 MHz): 7.45 (11

H, m, ArH), 6.28 (1 H, q, *J*/Hz: 2), 5.80 (1 H, q, *J*/Hz: 6), 2.20 (3 H, d, *J*/Hz: 2), 1.60 (3 H, s) and 1.45 (3 H, d, *J*/Hz: 6); *m*/*z* 342, 193, 178, 105 and 77 (6.5, 100.0, 26.5, 90.8 and 14.6%).

(−)-1-*Hydroxymethyl*-1,3-*dimethylbenz*[f]*indene* **17**.—A solution of the ester **16** (150 mg, 0.44 mmol) in tetrahydrofuran (19 ml) was cooled to −74 °C. After 10 min lithium aluminium hydride (74 mg, 1.9 mmol) was added in small portions, and the suspension stirred for 5 h before being warmed to room temperature. The mixture was diluted with water, dichloromethane and 1M sulphuric acid and the aqueous layer was separated and extracted with dichloromethane. The combined extracts were washed with brine, dried ($MgSO_4$) and evaporated to an oil (155 mg). Very careful chromatography on silica with hexane–ether (70:30) gave the *title compound* **17** as an oil (88 mg, 89%); $[\alpha]_D^{25}$ −66° (*c* 0.66 in $CHCl_3$) (Found: M^+, 224.121. $C_{16}H_{16}O$ requires: M, 224.120); ν_{max}/cm^{-1} (film) 3350, 2910 and 1030; δ_H(90 MHz) 7.50 (6 H, m, ArH), 6.05 (1 H, q, *J*/Hz: 2), 3.65 (2 H, s), 2.20 (3 H, d, *J*/Hz: 2), 1.70 (1 H, br s) 1.35 (3 H, s); *m*/*z* 224, 193, 178, 165 and 69 (18.5, 100.0, 41.2, 9.1 and 6.7%).

(−)-1,3-*Dimethylbenz*[f]*indene*-1-*carbaldehyde* **1**.—A solution of dimethyl sulphoxide (71.3 mg, 0.91 mmol) in dichloromethane (4 ml) was cooled to −78 °C. After 10 min oxalyl chloride (53 mg, 0.42 mmol) in dichloromethane (2 ml) was added, and the solution stirred for 5 min. A solution of compound **17** in dichloromethane (4 ml) was added dropwise, and after 20 min triethylamine (192.3 mg, 1.9 mmol) in dichloromethane (2 ml) was added. After 10 min the solution was allowed to warm slowly to room temperature. Water and dichloromethane were added, and the aqueous phase was extracted with dichloromethane. The combined extracts were washed with 1M hydrochloric acid, 1M aqueous sodium hydrogen carbonate and brine, dried ($MgSO_4$) and evaporated to give an oil (48 mg). Chromatography of this on silica with hexane–benzene gave **1** as oil (38.2 mg, 89%); $[\alpha]_D^{25}$ −214° (*c* 1.91, $CHCl_3$) (Found: M^+, 222.105. $C_{16}H_{14}O$ requires M, 222.104); ν_{max}/cm^{-1}(film) 1715; δ_H(90 MHz) 8.72 (1 H, s), 7.85 (2 H, m, ArH), 7.70 (2 H, s), 7.45 (2 H, m, ArH), 6.00 (1 H, q, *J*/Hz: 2), 2.30 (3 H, d, *J*/Hz: 2) and 1.55 (3 H, s): *m*/*z* 222, 210, 193, 178, 165, 152 and 89 (16.5, 21.4, 100.0, 56.3, 21.4, 12.1 and 11.7%).

Thermolysis of (±)-1,3-*Dimethylbenz*[f]*indene*-1-*carbaldehyde*.—A solution of the (±)-aldehyde **1** (16 mg, 0.07 mmol) in deuteriobenzene (*ca.* 0.04 ml) was degassed in a small bore tube and the tube sealed *in vacuo*. Heating at <230 °C induced no reaction observable by NMR. However, after 8 h and 12 min at 230 °C, no starting material remained and the major product could be identified by NMR as 1,3-dimethylbenz[*f*]indene. The 400 MHz spectrum allowed the identification of 3.4% of the indenecarbaldehyde **18** as well as starting material (64.4%) and the decarbonylation product **6** (32.2%), after thermolysis of 230 °C for 87 min.

Trapping of the Isoindene Intermediate **2** *with* N-*Phenylmaleimide*.—The carbaldehyde **1** (154 mg, 0.24 mmol), *N*-phenylmaleimide (208 mg, 1.2 mmol) and diphenyl ether (2 ml) were heated at 160 °C for 24 h, *N*-Phenylmaleimide (623 mg, 3.6 mmol) was then added, and heating at 160 °C continued for a total of 112 h. Chromatography of the mixture on silica with benzene–ether (85:15) gave the *syn-endo-adduct* **21** (34 mg, 36%) (Found: M^+, 395.153. $C_{26}H_{21}NO_3$ requires: M, 395.152); ν_{max}/cm^{-1}(Nujol) 1710, 1500, 1185 and 755; δ_H(90 MHz) 10.00 (1 H, d, *J*/Hz: 2), 7.35 (9 H, m, ArH), 5.95 (2 H, m), 3.65 (2 H, s), 2.98 (1 H, d, *J*/Hz: 2) and 2.00 (6 H, s); *m*/*z* 395, 222, 193, 178, 173 and 69 (45.2, 13.3, 100.0, 40.2, 6.1 and 6.0%). Further elution gave the anti-endo-*adduct* **20** (32 mg, 34%) (Found: M^+, 395.152. $C_{26}H_{21}NO_3$ requires 395.152); ν_{max}/cm^{-1}(Nujol) 1710, 1500 and 1185; δ_H(90 MHz), 9.05 (1 H, d, *J*/Hz: 4), 7.45 (9 H, m, ArH), 6.00 (2 H, m), 3.45 (2 H, s), 2.800 (1 H, d, *J*/Hz: 4) and 1.90 (6 H, s); *m*/*z* 395, 222, 193 and 178 (36.1, 7.3, 100.0 and 38.5%).

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