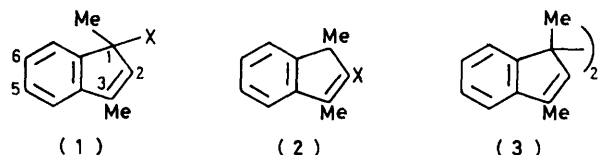


Radical Rearrangements of 1,3-Dimethylindene Derivatives: A Comparison with Rearrangement by 1,5-Sigmatropy

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Radical dissociation-recombination mechanisms are proposed for the following thermal reactions: (i) interconversion of the *meso*- and (\pm)-forms of the bi-indenyls (3) and (6), (ii) racemisation of the methyl ether (1; X = Ph₃COMe), and (iii) diastereoisomerisation of the optically active semithioacetals (10). The characteristics of these reactions stand in contrast to those of similar reactions following a concerted path.

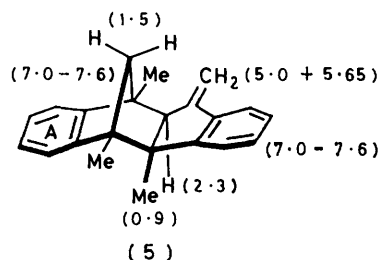
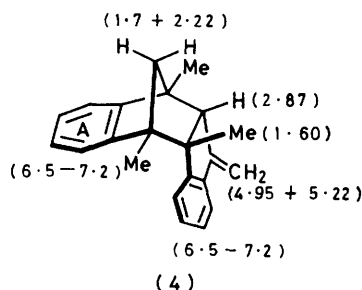
INDENES are useful substrates for testing the 1,5-sigmatropy of a variety of groups.^{1,2} Such rearrangement, involving two 1,5-shifts and a 2*H*-indene intermediate results, for example, in the movement of X in (1) from C-1 to C-3; an optically active derivative (1) would thereby be racemised. This same change could, in principle, occur by homolysis of the C(1)-X bond in (1) followed by recombination of the radicals at C-3 of the indene. The work described below was initiated to define the nature of X in (1) required to observe the



dissociation-recombination mechanism at moderate temperatures (< ca. 200 °C). Since 2-X-substituted indenenes (2), formed by 1,5-hydrogen shift in a 2*H*-indene intermediate, are regarded as characteristic products of the concerted rearrangement^{2a,d} it was of interest to examine the possibility that the radical rearrangement could also give rise to 2-substituted indenenes (2). Both the absence of cross-over products^{2a} and strict stereospecificity^{2d} characterise the concerted rearrangement; the radical rearrangement should provide instructive counterpoint in these respects.

We previously noted formation of a mixture of the *meso*- and (\pm)-forms of the bi-indenyl (3) upon reaction of 1,3-dimethylindenyl-lithium with *p*-nitrobenzoyl chloride.^{2a} A clean ca. 1 : 1 mixture of these diastereoisomers can be prepared in 90% yield by oxidation of 1,3-dimethylindenyl-lithium with either iodine or nitrobenzene. Short-column chromatography on silica allows separation of the diastereoisomers.† Configurations were assigned to the *meso*- and (\pm)-forms by their conversion in chloroform-trifluoroacetic acid to compounds (4) and (5) respectively. The ¹H n.m.r. spectra of compounds (4) and (5) show strong shielding of groups *cis* to the phenylene ring-A allowing firm assignment of stereochemistry [see δ -values appended to formulae (4) and (5)]. The *meso*- and (\pm)-bi-indenyls (3) were interconverted, rapidly in boiling xylene or toluene (<3 h), and slowly in boiling benzene (>36 h), to give a 1 : 2

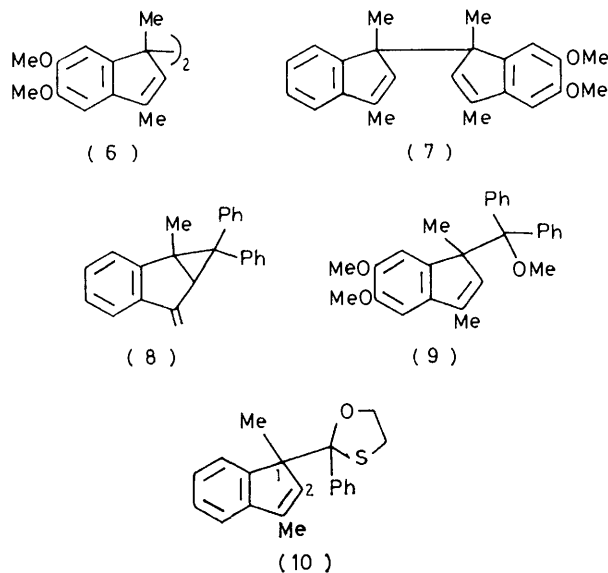
mixture of the *meso*- and (\pm)-forms. Since Cope rearrangement of either diastereoisomer is degenerate, diastereoisomerisation must involve either (a) two 1,5-shifts of one indenyl unit over its partner or (b) radical rearrangement. The very low tendency of alkyl groups to undergo 1,5-shift strongly favours rearrangement by a radical path. Indeed a mixture of the bi-indenyls (3) and tri-*n*-butyltin hydride in boiling xylene gave 1,3-dimethylindene (1; X = H). In full agreement with a radical mechanism, a mixture of the stereoisomers (3) and the analogous stereoisomers (6) when heated in



boiling xylene (1 h) gave the cross-over product (7) (36%) characterised by mass spectroscopy and its ¹H n.m.r. spectrum (see Experimental section). Decomposition of the *t*-butyl perester (1; X = CO₃Bu^t) in boiling benzene (1.5 h) gave the stereoisomeric bi-indenyls (3). However, the 1,3-dimethylindenyl radicals presumably generated as intermediates failed either to induce rearrangement of *meso*-(6) to its (\pm)-isomer or produce the cross-over product (7) from it. A radical-induced rearrangement³ of the bi-indenyls with the 1,3-dimethylindenyl radical as chain-carrier is therefore unlikely, and a dissociation-recombination process is indicated.

† Cf. P. Nicolet, J.-Y. Sanchez, and M. J. M. Abadie, *J. Chem. Soc., Chem. Commun.*, 1981, 347.

The kinetics of related radical rearrangement were conveniently investigated using the methyl ether (1; X = Ph₂COMe) prepared from the optically active acid (1; X = CO₂H)^{2b} via the acid chloride [(COCl)₂] and the carbinol (1; X = Ph₂COH). In boiling methanol containing toluene-*p*-sulphonic acid the carbinol gave the methyl ether (1; X = Ph₂COMe) which could be separated from the homofulvene (8) also formed, by silica chromatography. The methyl ether, [α]_D 131.45° [*c* 2.1 (CHCl₃)], was recovered in optically inactive form



together with traces of the bi-indenyls (3) after being heated in boiling toluene (1 h). No 2-substituted indene was detected. Racemisations of the methyl ether in diphenyl ether solution followed first-order kinetics and gave the following rate data: [10⁻⁵ k/s⁻¹ (T/°C)], 4.49 (87), 11.7 (95), 24.5 (102), 52.2 (109), Δ*H*‡ = 28.87 ± 0.3 kcal mol⁻¹, Δ*S*‡ = 1.46 ± 0.4 cal K⁻¹ mol⁻¹. The small positive activation entropy contrasts with the uniformly negative values, *ca.* -10 cal K⁻¹ mol⁻¹, observed for concerted 1,5-shifts of unsaturated groups in 1,3-dimethylindenes.^{2b,c} A radical mechanism for the racemisation is supported by formation of the cross-over products (7) (1 part) and (9) (2 parts) on heating (1; X = Ph₂COMe) and (6) together (140 °C, 1 h). The racemisation of (1; X = Ph₂COMe) was not speeded by a radical initiator (benzoyl peroxide, *k* = 3.0 ± 0.45 × 10⁻⁵/s⁻¹, 87 °C) or slowed by a radical inhibitor (*t*-butylcatechol, *k* = 2.9 × 10⁻⁴ s⁻¹, 102 °C) in agreement with a dissociation-recombination mechanism rather than the more commonly encountered radical-induced (chain) mechanism for rearrangement.³ Mechanisms for rearrangement involving ionic intermediates can be discounted for racemisation in dimethyl sulphoxide (*k* = 5.77 × 10⁻⁵/s⁻¹, 87 °C) is only 1.59 times more rapid than racemisation in decalin.

To investigate the stereochemistry of radical rearrangement we prepared the diastereoisomeric ethylene-

semithioacetals (10) [(A), [α]_D +33.7° and (B), [α]_D +108.8° (CHCl₃)] from (+)-1-benzoyl-1,3-dimethylindene.^{2b} Unlike other diastereoisomers tried the diastereoisomers (A) and (B) proved separable by careful short-column chromatography on Kieselgel G (Merck). In diphenyl ether solution at 170 °C (1 h) (+)-(A) gave *ca.* 25% of the diastereoisomer (B) ([α]_D -50.45°, CHCl₃) and recovered (A) ([α]_D +27.4°, CHCl₃). When similarly heated (+)-(B) gave *ca.* 25% (A) ([α]_D -14.91°) and recovered (B) ([α]_D +93.4°). Thus in both cases diastereoisomerisation involves >70% inversion of the indene stereo-centre and >70% retention at the acetal centre. This is consistent with homolysis of the indene C(1)-acetal bond to give a caged biradical intermediate⁴ followed by preferential recombination of the radicals at their originally bonded faces; combination at C-1 returns the starting diastereoisomer and combination at C-3 gives the (-)-diastereoisomer. The >25% loss of stereochemistry in the radical rearrangement contrasts with the stereospecificity observed in concerted rearrangement.^{2d}

In summary we have shown that for 1,3-dimethylindenes the dissociation-recombination process is only likely (below *ca.* 200 °C) if X [in (1)] is capable of forming a strongly stabilised radical. The radical rearrangement is distinguished from its concerted counterpart by the formation of cross-over products, by a failure to yield 2-substituted indenenes, by a more positive value of Δ*S*‡, and by non-stereospecificity.

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 R12 (60 MHz) or R32 (90 MHz) spectrometer. Mass spectra were obtained with an A.E.I. MS902 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 chromatography⁵ over Kieselgel G (Merck). Kinetic measurements were made as previously described.^{2b}

meso- and Racemic-1,1',3,3'-Tetramethyl-1,1'-bi-indenyl (3).—1,3-Dimethylindene (0.49 g) and ether (25 ml) were stirred at 0 °C under nitrogen and *n*-butyl-lithium (3.74 ml of 1.25M-solution in hexane) was added by syringe. After the mixture had been stirred for 30 min at 0 °C iodine (0.47 g) was added. The ice-bath was removed and the mixture stirred at room temperature (1 h). The product was diluted with ether and washed with sodium metabisulphite solution, washed with water, dried (MgSO₄) and evaporated to give a crystalline solid (460 mg). A portion of this solid (370 mg) was chromatographed on silica in petroleum-benzene (4 : 1) to give first *meso-1,1',3,3'-tetramethyl-1,1'-bi-indenyl* (171 mg), m.p. 135–136 °C (from chloroform-ethanol) (Found: C, 91.95; H, 6.7. C₂₂H₂₂ requires C, 92.3; H, 6.7%); ν_{max.} (Nujol) 1 620 cm⁻¹; λ_{max.} (EtOH) 263 nm (ε 14 632); δ 1.2 (6 H, s), 2.1 (6 H, d, *J* 2 Hz), 6.17 (2 H, q, *J* 2 Hz), and

7.1 (8 H, m, ArH). Continued elution of the column gave racemic 1,1',3,3'-tetramethyl-1,1'-bi-indenyl (154 mg), m.p. 108–109 °C (from chloroform-ethanol) (Found: C, 92.3; H, 6.7%), ν_{\max} (Nujol) 1 620 cm^{-1} ; λ_{\max} (EtOH) 261 nm (ϵ 14 300); δ 1.4 (6 H, s), 2.1 (6 H, d, *J* 2 Hz), 6.05 (2 H, q, *J* 2 Hz), and 7.0 (8 H, m, ArH). Between the two components a mixture of *meso* and racemic forms (42 mg) was eluted from the column.

When 1,3-dimethylindenyl-lithium prepared as above from 1,3-dimethylindene (200 mg) was treated with nitrobenzene (195 mg) at 0 °C and then at 20 °C (30 min) subsequent chromatography gave a mixture of the *meso*- and (\pm)-dimers (179 mg).

Cyclisation of *meso*- and Racemic-1,1',3,3'-Tetramethyl-1,1'-bi-indenyl with Trifluoroacetic Acid.—When the *meso*-isomer (26 mg) in deuteriochloroform (0.25 ml) and trifluoroacetic acid (100 mg) was set aside for 30 min the n.m.r. spectrum showed the absence of starting material. The product was diluted with ether and washed successively with saturated sodium hydrogen carbonate solution and water and then dried (MgSO_4) and evaporated. The crystalline product (22 mg) was sublimed at 81 °C (0.01 mmHg) to yield the *benzonorbornane* (4) (18 mg), m.p. 127–128 °C (Found: C, 92.3; H, 6.7%), ν_{\max} (Nujol) 1 635 cm^{-1} ; λ_{\max} (EtOH) 263 nm (ϵ 10 868); δ 1.57 (9 H, m, 3 \times Me), 1.7 (1 H, d, *J* 6 Hz, AB system), 2.22 (1 H, d, *J* 6 Hz, AB system), 2.87 (1 H, m), 4.95 (1 H, d, *J* 2 Hz, olefinic), 5.22 (1 H, d, *J* 2 Hz, olefinic), and 6.5–7.2 (8 H, m, ArH).

Treatment of the racemic isomer (22 mg) as above gave after sublimation at 91 °C (0.01 mmHg) the *benzonorbornane* (5) (14 mg), m.p. 104–105 °C (Found: C, 92.3; H, 6.7%), ν_{\max} (Nujol) 1 630 cm^{-1} ; λ_{\max} (EtOH) 260 nm (ϵ 9 640); δ 0.9 (3 H, s), 1.5 (8 H, m), 2.3 (1 H, m), 5.0 (1 H, d, *J* 2 Hz), 5.65 (1 H, d, *J* 2 Hz), and 7.0–7.6 (8 H, m, ArH).

5,5',6,6'-Tetramethoxy-1,1',3,3'-tetramethyl-1,1'-bi-indenyl (6).—5,6-Dimethoxy-3-methylindan-1-one (20 g) in ether (400 ml) was slowly added to an ethereal solution of methylmagnesium iodide [from magnesium (6.98 g) and methyl iodide (42 g) in ether (150 ml)]. After completion of the addition and stirring for 1 h at 20 °C the product was shaken with saturated ammonium chloride solution and then 2*N*-hydrochloric acid (100 ml). The ether solution was dried (MgSO_4) and evaporated and the crude product (16 g) distilled bulb-to-bulb (130 °C, 0.01 mmHg) to give 5,6-dimethoxy-1,3-dimethylindene (12 g), m.p. 65 °C (Found: C, 76.4; H, 7.8. $\text{C}_{13}\text{H}_{16}\text{O}_2$ requires C, 76.5; H, 7.8%), ν_{\max} (Nujol) 1 602 cm^{-1} ; λ_{\max} (EtOH) 267, 300, and 305 nm (ϵ 14 690, 4 491, and 4 100); δ 1.25 (3 H, d, *J* 6 Hz), 2.15 (3 H, m), 3.35 (1 H, m), 4.92 (6 H, s, OMe), 6.05 (1 H, m), 6.85 (1 H, s, ArH), and 7.0 (1 H, s, ArH). The foregoing indene (600 mg) in ether (30 ml) was treated with *n*-butyllithium (2.5 ml of a 1.2*M*-solution in hexane) with stirring under a nitrogen atmosphere at 20 °C. After the mixture had been stirred for 30 min nitrobenzene (480 mg) was added to it and the stirring continued (30 min). The crude product (1.025 g), isolated in ether, was chromatographed on alumina in ether-benzene (7:93) to give a mixture (410 mg) of the *meso*- and (\pm)-bi-indenyls (6). Trituration with ether (10 ml) allowed separation of these diastereoisomers. The ether-insoluble portion (250 mg), m.p. 132–134 °C (from benzene-petroleum) is tentatively assigned as the (\pm)-form (Found: C, 76.9; H, 7.5. $\text{C}_{26}\text{H}_{30}\text{O}_4$ requires C, 76.85; H, 7.4%), ν_{\max} (Nujol) 1 602 cm^{-1} ; δ 1.3 (6 H, s), 1.87 (6 H, m), 3.67 (6 H, s), 3.81 (6 H, s), 5.92 (2 H, m), 6.4 (2 H, s), and 6.6 (2 H, s). The ether-

soluble portion (156 mg), m.p. 116–119 °C (from benzene-petroleum) is tentatively assigned as the *meso*-form (6) (Found: C, 76.8; H, 6.8%), ν_{\max} (Nujol) 1 602 cm^{-1} ; δ 1.35 (6 H, s), 2.25 (6 H, m), 4.67 (6 H, s), 4.8 (6 H, s), 6.15 (2 H, m), 6.45 (2 H, s), and 6.7 (2 H, s).

(-)-1-(Hydroxydiphenylmethyl)-1,3-dimethylindene.—(-)-1,3-Dimethylindene-1-carboxylic acid (2.1 g) { $[\alpha]_{\text{D}} - 68.8^\circ$ (CHCl_3)}^{2b} and oxalyl chloride (20 ml) were stirred at -5 °C in a nitrogen atmosphere (2 h). Excess of reagent was removed *via* a water-pump vacuum and the acid chloride (2.3 g) in ether (30 ml) added dropwise to phenylmagnesium bromide [from bromobenzene (14 g) and magnesium (2.14 g) in ether (100 ml)] cooled to 0 °C in a nitrogen atmosphere. After the addition the product was stirred at 0 °C (1.5 h) and worked up by careful addition of saturated aqueous ammonium chloride at 0 °C. The ether layer was washed with water, dried (MgSO_4), and evaporated at 20 °C under reduced pressure. Chromatography on silica in benzene-petroleum (9:1) gave crude 1-(hydroxydiphenylmethyl)-1,3-dimethylindene (1; X = Ph_2COH) which was recrystallised from chloroform-ethanol to give pure material (1.35 g), $[\alpha]_{\text{D}} - 74.6^\circ$ (CHCl_3), δ 1.4 (3 H, s), 2.02 (3 H, d, *J* 2 Hz), 1.6 (1 H, s, OH), 6.27 (1 H, q, *J* 2 Hz), and 7.0–7.5 (14 H, m), ν_{\max} (Nujol) 3 580 (sharp). A small sample of the alcohol prepared from optically pure (-)-1,3-dimethylindene-1-carboxylic acid had $[\alpha]_{\text{D}} - 78.6^\circ$ (CHCl_3). The magnesium derivative of the product alcohol is susceptible to racemisation. The temperature of the reaction mixture should, therefore, be carefully maintained at 0 °C and the product quenched carefully and without undue delay. A sample of the alcohol was prepared from optically pure (+)-1-benzoyl-1,3-dimethylindene (124 mg) by addition to phenylmagnesium bromide [from magnesium (72 mg) and bromobenzene (471 mg) in ether (5 ml)] at 0 °C. After being stirred at 0 °C (1.5 h) the reaction mixture was allowed to warm to 20 °C over 30 min when it acquired a pink colour which faded on cooling to 0 °C prior to work-up as previously described; chromatography on silica in benzene-petroleum (7:3) gave 1-(hydroxydiphenylmethyl)-1,3-dimethylindene (145 mg), $[\alpha]_{\text{D}} + 55^\circ$ (*c* 1.4, CHCl_3). When the reaction was repeated but the reaction mixture was stirred at 20 °C (16 h) before aqueous work-up the alcohol obtained was optically inactive.

(+)-1-(Methoxydiphenylmethyl)-1,3-dimethylindene.—The foregoing alcohol (145 mg), $[\alpha]_{\text{D}} + 55^\circ$ (*c* 1.4, CHCl_3), methanol (10 ml), and toluene-*p*-sulphonic acid (5 mg) were boiled under reflux in a nitrogen atmosphere (16 h). The product was poured into water and extracted with dichloromethane. The organic layer was washed successively with saturated aqueous sodium hydrogen carbonate and water, dried (MgSO_4) and evaporated; the product was chromatographed on silica (50 g) in benzene-petroleum (15:85) to give 1-(methoxydiphenylmethyl)-1,3-dimethylindene (50 mg) as an oil, δ (90 MHz) 1.2 (3 H, s), 1.87 (3 H, d, *J* 2 Hz), 3.0 (3 H, s), 6.12 (1 H, q, *J* 2 Hz), and 6.8–7.6 (14 H, m); ν_{\max} (film) 1 618, 1 597, 1 576, and 1 065 br cm^{-1} ; *m/e* 197.096 ($\text{Ph}_2\text{C}=\text{OMe}$ requires 197.097), 183, 182, 144, 143, 142, 141, 129, 128, and 105 (54.6, 54.2, 36.1, 40.2, 28.6, 16.3, 18.3, 36.4, 28.8, 100%) (peaks below *m/e* 100 and of less than 10% relative abundance not quoted; the molecular ion was absent); $[\alpha]_{\text{D}} + 131.45^\circ$ (*c* 2.1, CHCl_3). Continued elution of the column gave a compound (36 mg), tentatively identified as the *homofulvene* (8), as an unstable oil (Found: M^+ , 308.155. $\text{C}_{24}\text{H}_{20}$ requires M^+ , 308.156), ν_{\max} (film)

1 659, 1 640, 1 600, and 1 578 cm^{-1} ; δ (90 MHz) 1.5 (3 H, s), 2.17 (1 H, s), 5.4 (1 H, s), 5.51 (1 H, s), and 6.8—7.6 (14 H, m).

1-t-Butylperoxycarbonyl-1,3-dimethylindene.—1,3-Dimethylindene-1-carboxylic acid was converted into the crude acid chloride as described above. This product (460 mg) in ether (5 ml) was added to a stirred mixture of sodium *t*-butyl peroxide (500 mg) and ether (7 ml) maintained at -5°C in a nitrogen atmosphere. After the mixture had been stirred for 1.5 h at -5°C the product was diluted with ether (25 ml) and washed with cold (10°C) saturated brine. The dried (MgSO_4) organic layer was evaporated at 20°C and excess of *t*-butyl hydroperoxide was removed at 20°C in a high vacuum to give the fairly pure *t*-butyl peroxyester (293 mg), δ (60 MHz) 1.1 (9 H, s, Bu^t), 1.57 (3 H, s), 2.08 (3 H, d, J 2 Hz), 6.07 (1 H, q, J 2 Hz), and 7.1—7.4 (4 H, m); ν_{max} (film) 1 780 cm^{-1} .

The Diastereoisomeric Ethylene Semithioacetals (10) of (+)-1-Benzoyl-1,3-dimethylindene.—(+)-1-Benzoyl-1,3-dimethylindene^{2b} (300 mg), toluene-*p*-sulphonic acid hydrate (100 mg), 2-mercaptoethanol (2 g), and benzene (40 ml) were boiled under reflux with water removal (36 h). The filtered product was diluted with ether and washed successively with sodium carbonate solution ($\times 2$) and water, and then dried (MgSO_4) and evaporated; the product was chromatographed on silica (100 g) in benzene to give a mixture of the semithioacetals (211 mg) which was subsequently separated by careful chromatography on silica in benzene-petroleum (35:65). The less-polar diastereoisomer (A) (Found: M^+ , 308.123. $\text{C}_{20}\text{H}_{20}\text{OS}$ requires M^+ , 308.123), m/e 167, 166, 165, 143, 142, 141, 129, 128, 127, 121, 115, and 105 (66, 100, 100, 31.8, 24.9, 28.8, 12.0, 63.1, 10.3, 13, 10.9, and 100%) (only $m/e > 100$ with relative abundance $> 10\%$ quoted); δ (90 MHz), 1.56 (3 H, s), 1.90 (3 H, d, J 1.5 Hz), 2.85—3.3 (2 H, m, CH_2S), 3.6—4.0 (1 H, m, CH_2O), 4.37—4.60 (1 H, m, CH_2O), 6.06 (1 H, q, J 1.5 Hz), 6.70—7.25 (8 H, m), and 7.45—7.70 (1 H, m); $[\alpha]_{\text{D}} + 33.7^\circ$ (*c* 0.94 CHCl_3). The more-polar diastereoisomer (B) (Found: M^+ , 308.122), m/e 165, 166, 167, 141, 142, 143, 129, 128, 127, 115, and 105 (100, 10.7, 4.2, 8.9, 6.0, 3.4, 4.6, 12.3, 2.1, 3.5, and 62.6%); δ (90 MHz) 1.34 (3 H, s), 1.96 (3 H, d, J 1.5 Hz), 2.65—2.94 (2 H, m, CH_2S), 3.60—3.92 (1 H, m, CH_2O), 4.30—4.56 (1 H, m, CH_2O), 5.98 (1 H, q, J 1.5 Hz), 6.70—7.4 (8 H, m), and 7.55—7.75 (1 H, m); $[\alpha]_{\text{D}} + 108.8^\circ$ (*c* 0.6 CHCl_3).

Thermolysis of meso- and Racemic-1,1',3,3'-Tetramethyl-1,1'-bi-indenyl.—The racemic bi-indenyl (48 mg) and xylene (2 ml) were boiled under reflux in a nitrogen atmosphere (2 h). Evaporation of solvent under reduced pressure on a water-bath gave a mixture of *meso*- and (\pm)-bi-indenyls (ratio 1:2) (n.m.r.); this ratio was unchanged on further heating in boiling xylene (1.5 h). On similar treatment the *meso*-bi-indenyl (45 mg) gave a similar 1:2 mixture of the *meso*- and (\pm)-diastereoisomers. The products of the two reactions were combined and chromatographed on silica in petroleum-benzene (4:1) to give the pure (\pm)-isomer (35 mg) and the pure *meso*-isomer (21 mg). Thermolysis of either diastereoisomer in toluene (3 h) also gave the equilibrium mixture, but thermolysis in benzene failed to produce the equilibrium mixture from either diastereoisomer after 37 h. A 1:1 mixture of the *meso*- and racemic isomers was obtained when the *meso*-isomer (50 mg) in deoxygenated acetonitrile (10 ml) in a quartz flask was placed 2 cm from the water-cooled jacket of a Hanovia 100-W medium-pressure mercury lamp (30 min).

Thermolysis and Photolysis of (\pm)-5,5',6,6'-Tetramethoxy-1,1',3,3'-tetramethyl-1,1'-bi-indenyl.—The title compound (83 mg) and xylene (10 ml) were boiled under reflux (30 min). N.m.r. and t.l.c. indicated a 2:1 mixture of the racemic- and *meso*-isomers. Irradiation of the (\pm)-dimer in deoxygenated acetonitrile (30 min) as described above gave a 1:1 mixture of the *meso*- and (\pm)-isomers (n.m.r.).

Thermolysis of (+)-1-(Methoxydiphenylmethyl)-1,3-dimethylindene.—The title compound {50 mg, $[\alpha]_{\text{D}} + 131.45$ (*c* 2.1, CHCl_3)} and toluene (10 ml) were boiled under reflux in a nitrogen atmosphere (65 min). Evaporation of toluene under reduced pressure on a water-bath gave a crude product (40 mg) devoid of optical activity and shown by n.m.r. to be mainly (\pm)-1-(methoxydiphenylmethyl)-1,3-dimethylindene.

Cross-over Experiments.—(a) A mixture of *meso*- and (\pm)-1,1',3,3'-tetramethyl-1,1'-bi-indenyl (61 mg) and *meso*- and (\pm)-5,5',6,6'-tetramethoxy-1,1',3,3'-tetramethyl-1,1'-bi-indenyl (82 mg) and xylene (10 ml) were boiled under reflux in a nitrogen atmosphere (1 h). Chromatography of the evaporated product on silica in benzene-ether (49:1) gave first recovered *meso*- and (\pm)-1,1',3,3'-tetramethylbi-indenyl (25 mg). Continued elution gave a mixture of the two diastereoisomeric forms of the crossed product, 5,6-dimethoxy-1,1',3,3'-tetramethyl-1,1'-bi-indenyl (63 mg). The mass spectrum of this product showed a molecular ion at m/e 346 (4.9%) and a base peak at m/e 203 (100%, 5,6-dimethoxy-1,3-dimethylindenyl cation) and m/e 143 (11.3%, 1,3-dimethylindenyl cation); a mechanical mixture of the bi-indenyls (3) and (6) showed peaks at m/e 406 (10.2%), 203 (100%), and 143 (29.1%) but no peak at m/e 346 was detected. The n.m.r. spectrum (60 MHz) of the cross-over product showed it to be a *ca.* 2:1 mixture of diastereoisomers: δ 1.2—1.45 (6 H, $\text{Me}=\text{C}$); 1.86, 2.0, 2.08 (6 H, d's, J *ca.* 2 Hz, $\text{Me}=\text{C}$); 3.57, 3.74, 3.76, 3.85 (6 H, s's, ratio *ca.* 2:1:1:2, OMe), 5.85—6.2 (2 H, olefinic), and 6.5—7.3 (6 H, ArH).

Elution of the column with benzene-ether (85:15) gave a mixture of the *meso*- and (\pm)-forms of 5,5',6,6'-tetramethoxy-1,1',3,3'-tetramethyl-1,1'-bi-indenyl (33 mg).

(b) 1-(Methoxydiphenylmethyl)-1,3-dimethylindene (70 mg) and a stereoisomeric mixture of 5,5',6,6'-tetramethoxy-1,1',3,3'-tetramethyl-1,1'-bi-indenyls (65 mg) were heated in boiling xylene (10 ml) (1 h) in a nitrogen atmosphere. Chromatography on silica in benzene-ether (99:1) gave a fraction of intermediate polarity (40 mg) which was not separable into its components by t.l.c. The 60 MHz ^1H n.m.r. spectrum of the mixture indicated the presence of the cross-over product (7) (1 part) and 1-(methoxydiphenylmethyl)-5,6-dimethoxy-1,3-dimethylindene (9) (2 parts). Proton resonances due to this latter compound are δ 1.2 (3 H, s, MeC), 1.85 (3 H, d, J *ca.* 2 Hz, MeC=), 3.05 (3 H, s, OMe), 3.8 (3 H, s, OMe), 3.9 (3 H, s, OMe), 6.05 (1 H, q, J *ca.* 2 Hz), 6.7 (1 H, s, ArH), and 6.9—7.5 (11 H, m, ArH). Early fractions from the chromatography gave recovered 1-(methoxydiphenylmethyl)-1,3-dimethylindene (40 mg) and later chromatography fractions gave recovered (\pm)- and *meso*-5,5',6,6'-tetramethoxy-1,1',3,3'-tetramethyl-1,1'-bi-indenyl (30 mg).

Thermolysis of 1-t-Butylperoxycarbonyl-1,3-dimethylindene.—The perester (265 mg) and deoxygenated benzene (25 ml) were boiled under reflux in a nitrogen atmosphere (1 h). Chromatography of the product (128 mg) on silica in petroleum-benzene (4:1) gave first *meso*-1,1',3,3'-tetra-

methyl-1,1'-bi-indenyl (15 mg) and then (\pm)-1,1',3,3'-tetramethyl-1,1'-bi-indenyl (13 mg).

When the perester (50 mg) was decomposed in boiling benzene (5 ml) in the presence of *meso*-5,5',6,6'-tetramethoxy-1,1',3,3'-tetramethyl-1,1'-bi-indenyl (25 mg) (1.5 h) the ^1H n.m.r. spectrum of the evaporated product showed the absence of both the cross-over product (7) and (\pm)-5,5',6,6'-tetramethoxy-1,1',3,3'-tetramethylbi-indenyl.

Thermolysis of the Ethylene Semithioacetals of (+)-1-Benzoyl-1,3-dimethylindene.—When the diastereoisomer (A) (70 mg) in diphenyl ether (0.25 ml) was heated in an n.m.r. tube at 170 °C for 1 h the ^1H n.m.r. spectrum indicated *ca.* 25% conversion into the diastereoisomer (B). The mixture was chromatographed on silica (50 g) in petroleum-benzene (7 : 3) to give first recovered diastereoisomer (A) (36.5 mg), $[\alpha]_{\text{D}} + 27.4^\circ$ (*c* 3.65, CHCl_3), then a mixture of both diastereoisomers (10 mg), and then diastereoisomer (B) (11.1 mg), $[\alpha]_{\text{D}} - 50.45^\circ$ (*c* 1.11, CHCl_3). Similar heating of the diastereoisomer (B) (85 mg) in diphenyl ether (0.25 ml) at 170 °C (65 min) followed by chromatography as described above gave the diastereoisomer (A) (16.3 mg), $[\alpha]_{\text{D}} - 14.91^\circ$ (*c* 1.63, CHCl_3) and recovered diastereoisomer (B) (55.1 mg), $[\alpha]_{\text{D}} + 93.4^\circ$ (*c* 5.51, CHCl_3). Rearrangement of diastereoisomer (B) in benzonitrile was not markedly more rapid (<2) than rearrangement in diphenyl ether. The purity of recovered products was carefully checked by t.l.c. and ^1H n.m.r. measurements.

*Reaction of 5,5',6,6'-Tetramethoxy-1,1',3,3'-tetramethyl-1,1'-bi-indenyl with Tri-*n*-butyltin Hydride.*—The *meso*- form of the title compound (46 mg), xylene (10 ml), and tri-*n*-butyltin hydride (350 mg) were heated under reflux in a nitrogen atmosphere (1 h). The total crude product was directly applied to a silica column in benzene; elution with benzene containing increasing quantities of ether gave 5,6-dimethoxy-1,3-dimethylindene (24 mg) identical (n.m.r. spectrum) with authentic material prepared earlier. On similar reduction the (\pm)- and *meso*-diastereoisomers of 1,1',3,3'-tetramethyl-1,1'-bi-indenyl gave 1,3-dimethylindene.

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