Migratory Tendencies for 1,5-Sigmatropic Shifts in the 1,3-Dimethylindene System

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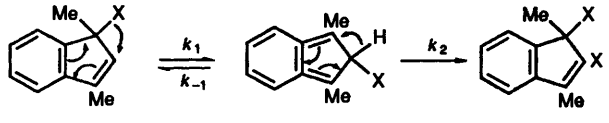
The tendency for several groups X to undergo a 1,5-sigmatropic shift in which **1** is converted into **2** has been tested. Several of the groups studied are based on the carbon–nitrogen double bond [HC=NBu^t, HC=NPh, HC=NNMe$_2$, 2-pyridyl and 1-methylpyridin-2-io], some were expected to be fast migrators (HC=CHNO$_2$, COCOPh, COSPh, C(S)NMe$_2$, and others (1- and 2-naphthyl, 2-furyl, 2-thienyl and 1-propylpyrrol-2-yl), showed a variation in aromatic character. The conjugative electron-withdrawing ability of a group and the availability of a low-energy vacant orbital are linked to good migratory ability but steric, conformational and secondary orbital interaction effects can mask the effect, *e.g.* the 1- and 2-naphthyl groups migrate slowly despite very low π^* energies. All the aromatic groups migrate slowly and at similar rates. The results provide further evidence against biradical intermediates or transition states of type **6** in these rearrangements.

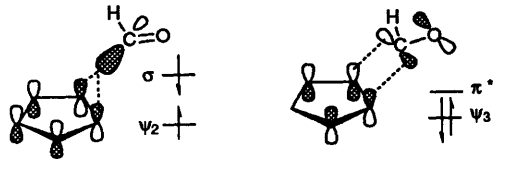
Optically active 1,3-dimethylindenes **1** are useful substrates for measuring the migratory tendencies of a variety of groups X in the 1,5-sigmatropic shift **1** (arrows) (Scheme 1). When the migration of X is slower than that of hydrogen in the 2*H*-indene intermediate **2** ($k_2 > k_{-1}$) the rate of formation of **3** is a good



1 **2** **3**

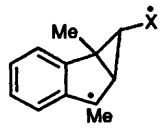
Scheme 1

measure of migratory ability but if X migrates faster than hydrogen in **2** ($k_{-1} > k_2$) the rate of formation of **3** underestimates the migratory ability of X. In the latter case, *e.g.* X = HCO, or Ac, the rate of racemisation of optically active indenes **1** *via* the symmetric 2*H*-indenes **2** provides good k_1 values. In this way the following order of migratory aptitude was established:[1a,b] HCO > Ac > H > vinyl > CO_2Me > C≡N ≈ C≡CH > Ph > Alk. Following Woodward and Hoffmann[2] the transition state (TS) for these shifts can be modelled as involving interaction of a formyl radical and a cyclopentadienyl radical as shown in **4**.



4 **5**

For an unsaturated migrating group there is a secondary interaction (see **5**) involving the vacant π^* orbital of that group and cyclopentadienyl ψ_3 (degenerate with ψ_2). This accounts for the greater migratory aptitude of unsaturated over saturated groups and, at least in part, rationalises the order of migratory aptitude HCO > Ac > CO_2Me as due to increasing energy of the π^* orbital. Steric and other orbital interactions may also be involved for these groups and greater strain in bridged TS's slows migration of triple bonded groups in cyclopentadienes[1c] but not in cycloheptatrienes.[1d] The present study sought to obtain migratory aptitudes for several unsaturated groups not previously examined. These were selected to further test correlation of migratory tendency with LUMO(π^*) energy of the migrating group. At the same time we have further examined[1e] the very slow migration of aromatic groups and provided further evidence against the suggestion[3] that rearrangement involves a bridged biradical TS or intermediate of type **6**.



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Preparation of 1-Substituted 1,3-Dimethylindenes.—The optically active imines **1** (X = CH=NBu^t) and **1** (X = CH=NPh), and the dimethylhydrazone **1** (X = CH=NNMe$_2$) were prepared from the known[1a] aldehyde **1** (X = CHO). The α-diketone **1** (X = COCOPh) was obtained from the acid chloride **1** (X = COCl) by reaction with the lithium salt of 2-phenyl-1,3-dithiane to give **7** and oxidative hydrolysis of the propylene dithioacetal (*N*-chlorosuccinimide, $AgNO_3$). The thioester **1** (X = COSPh) was prepared from the acid **1** (X = CO_2H)[1a] by reaction with thiophenol in the presence of phenyl dichlorophosphate and pyridine.[4] The thioamide **1** [X = C(S)NMe$_2$] was formed by reaction of the amide **1** (X = CONMe$_2$) with Lawesson's reagent in boiling toluene. Reaction of the optically active aldehyde **1** (X = CHO) with the lithium salt of (*E*)-but-2-enyldiphenylphosphine oxide[5] gave the diene **1** [X = (*E*,*E*)-penta-1,3-dienyl].

The pyridine **1** (X = 2-pyridyl) was prepared by acid-catalysed cyclisation of the bis-oxime **8** (X = X^1 = NOH) prepared from the keto acetal **8** [(X = O, X^1 = (OMe)$_2$]. The latter was formed by oxidation (CrO_3·2Py–CH_2Cl_2) of the alcohol **8** [X = H, OH; X^1 = (OMe)$_2$] obtained from the Grignard reagent **9** and the aldehyde **1** (X = CHO). With trimethyloxonium tetrafluoroborate the pyridine gave the *N*-methylpyridinium salt **10**.

The naphthalene **1** (X = 2-naphthyl) was simply prepared by the reaction of the lithium salt of 1,3-dimethylindene with 2-bromonaphthalene. 1-Bromonaphthalene gave the same product and in that case the yield improved when the reaction was conducted in the dark. Accordingly, the originally conceived SR_Nl mechanism[6] does not apply, rather a 2-naphthalyne

Table 1 Rate data for rearrangement of groups based on the carbon–nitrogen double bond

Indene **1** X =	$10^5 k/s^{-1}$ (T/°C) $\Delta H^{\ddagger}$/kcal mol^{-1} $\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	Solvent	Method/notes
(i) HC = NBu^t	3.93 (170)	C_6D_6	P_1
(ii) HC = NPh	13.26 (170)	C_6D_6	P_1
(iii) HC = $NNMe_2$	4.66 (200), 9.05 (210), 16.2 (220), 36.3 (230) $\Delta H^{\ddagger}$ = 30.87 ± 1.79 $\Delta S^{\ddagger}$ = −14.07 ± 3.68	Ph_2O	P_M
(iv) 2-Pyridyl	2.94 (286)	Ph_2O	NMR
(v) 1-Methylpyridin-2-io	No rearrangement detected at 240 °C (NMR) and no loss of optical activity after 2 h at 200 °C	MeCN	NMR + P_1
(vi) (*E*)-HC=CHPh	1.28 (180)	Ph_2O	Ref. 1[a]
(vii) HC=O	5480 (140)	Ph_2O	Ref. 1[a]
(viii) Ph in 1-methyl-1-phenylindene	8.0 (300)	Ph_2O	Ref. 10

[a] P_1 = Polarimetric one-point rate constants; P_M = polarimetric multiple-point rate constant; NMR = rate constant from NMR spectrum integrals.

intermediate is involved. 3-Methylindenone **11** and lithium di(1-naphthyl)cuprate gave the indanone **12** which with methylmagnesium iodide and dehydration of the resulting alcohol was converted into **1** (X = 1-naphthyl). In a similar way **1** (X = 2-furyl) and **1** (X = 2-thienyl) were obtained starting with **11** and the appropriate 2-lithio heterocycle. The pyrrole **13** was obtained in optically active form. Addition of the Grignard reagent **14**[7] to **1** (X = CHO) followed by oxidation (CrO_3·2Py–CH_2Cl_2) gave the keto acetal **15** [X = $O(CH_2)_2O$] which with potassium periodate in acid solution[8] gave the keto aldehyde **15** (X = O). Acid-catalysed condensation of the latter with propylamine[9] then gave the pyrrole **13**.

Migration of Groups based on the Carbon–Nitrogen Double Bond.—The 1,5-migration of both carbon–oxygen double-bonded groups and the generally slower migration of carbon–carbon double-bonded groups have been studied[1a,b] and the ease of migration of vinyl groups with *E* electron-withdrawing substituents has been shown to increase as the resonance electron-withdrawing ability of the *E* substituent increases.[1b] The migration of carbon–nitrogen double-bonded groups would, therefore, be expected to proceed at rates between those for similarly substituted C=C and C=O groups. Comparison of entries (i) and (ii) with entries (vi) and (vii) in Table 1 supports this view. The easy hydrolysis of the imines **1** (X = CH=NBu^t) and **1** (X = HC=NPh) to give the rapidly racemised aldehyde **1** (X = CHO) meant that thermolysis had to be carried out under strictly anhydrous conditions. The freshly distilled amines in dried C_6D_6 were degassed and the sealed NMR tubes heated at 170 °C with ^{1}H NMR monitoring of reaction progress. When an appropriate amount of the 2-isomer **3** had accumulated the optical rotation of the solution was obtained and used to provide the one-point rate constants given in Table 1 [entries (i) and (ii)]. In both cases small quantities of the aldehyde **1** (X = CHO) appeared during thermolysis. If a fast exchange process occurred between imine and aldehyde **1** (X = CHO) a major part of the racemisation could occur *via* the 1,5-formyl shift in **1** (X = CHO). An estimate of the exchange rate between **1** (X = CDO) and **1** (X = HC=NPh) [giving **1** (X = CHO) and **1** (X = DC=NPh)] was obtained by heating equimolar quantities of these compounds at 170 °C in dry C_6H_6 and following the exchange by ^{2}H NMR. When the maximum aldehyde concentration (10%) observed even in prolonged reactions is used as the standing concentration an exchange rate < 0.05 of the racemisation rate is observed (see Experimental section). Rearrangement of the relatively hydrolytically stable dimethylhydrazone **1** (X = HC=$NNMe_2$) proceeded cleanly at higher temperatures to give the rate data and derived activation parameters shown [entry (iii) Table 1]. The negative activation entropy agrees with values obtained for C=O and C=C migration and supports concerted rearrangement. Slower migration of HC=N–NMe_2 than HC=NBu^t and HC=NPh is expected. Resonance involving the nitrogen lone pair in the hydrazone group will reduce the resonance electron-accepting ability of the carbon–nitrogen double bond (or raise the π* orbital energy). A similar effect is observed for the CO_2Me group although further orbital interaction involving the alkoxy oxygen may be partly responsible for the very slow migration of this group.[1a] The *E*-HC=CHCl group migrates too slowly in the indene system for accurate kinetic measurements.[1b] The slower migration of HC=N–NMe_2 than HC=NBu^t provides evidence against a biradical **6** (X = N–NMe_2) as TS or intermediate in the rearrangement; hydrazyl radical character **16** would be expected to stabilise such an entity and speed rearrangement.

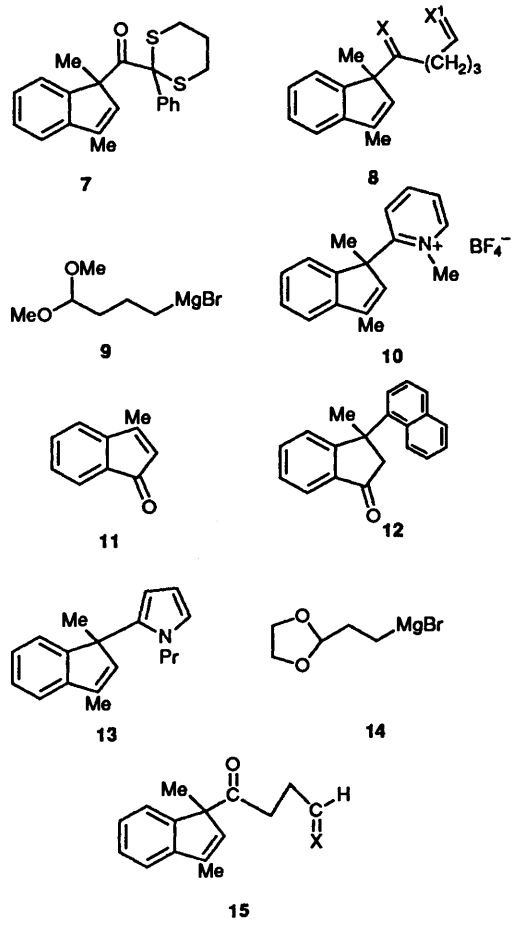

Table 2 Rate data for rearrangement of groups of low π* orbital energy

Indene **1** X =	$10^5\ k/s^{-1}$ (T/°C) $\Delta H^{\ddagger}$/kcal mol^{-1} $\Delta S^{\ddagger}$/cal deg^{-1} mol^{-1}	Solvent	Method/notes[a]
(i) (*E*,*E*)-HC=CHCH=CHMe	7.72 (200)	C_6D_6	P_I
(ii) PhSCO	10.33 (190)	Ph_2O	P_M
(iii) (*E*)-CH=CHNO$_2$	10.9 (170), 15.8 (175), 21.9 (180, 29.9 (185) $\Delta H^{\ddagger} = 26.08 \pm 0.56$ $\Delta S^{\ddagger} = -18.53 \pm 1.25$	Ph_2O	P_M
(iv) (E)-CH=CHNO$_2$	5.8 (150)	DMSO	P_M
(v) COCOPh	57.1 (120)	Ph_2O	P_M
(vi) HC=CH$_2$	1.79 (210)	Ph_2O	Ref. 1*b*
(vii) PhOCO	1.65 (225)	Ph_2O	Ref. 1*a*
(viii) (*E*)-CH=CHCOPh	34.94 (180)	Ph_2O	Ref. 1*b*
(ix) (*E*)-CH=CHCHO	9.94 (170)	Ph_2O	Ref. 1*b*
(x) PhCO	58.07 (170)	Ph_2O	Ref. 1*b*

[a] See footnote for Table 1.

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Migration of a 2-pyridyl group was examined in the expectation that rearrangement would be more rapid than for the previously tested phenyl group.[10] However, entries (iv) and (v) (Table 1) shows these groups migrate at very similar rates. Even more striking is the failure of the pyridinium group in **10** to rearrange below 240 °C at which temperature general decomposition began [Table 1, entry (v)]. Whatever factor(s) is (are) responsible for the very slow migration of even feebly aromatic groups (see below) it (they) appears (appear) to exert a levelling effect that masks the normally observed influence of resonance electron withdrawal.

Rearrangement of Potentially Good Migrators.—In entries (i)–(v) of Table 2 we collect migratory aptitude data for groups which were expected, largely on the basis of resonance electron-withdrawing ability or low π*-orbital energy, to be better migrators than the comparison groups in entries (vi)–(x) of the Table. Thus the penta-1,3-dienyl group [entry (ii)] with a lower π* energy than vinyl migrates *ca.* 10 times faster than the vinyl group [entry (vi)] and at a rate comparable to that of the *E*-styryl group [Table 1, entry (vi)].

The thioester group (PhSCO) of entry (ii), Table 2, migrates *ca.* 70 times faster than the ester group (PhOCO) of entry (vii). This agress with a lower $\pi^*_{C=O}$ energy in the thioester due to reduced interaction between the sulfur lone-pair orbital (3p) and the carbon 2p orbital at the carbonyl carbon.

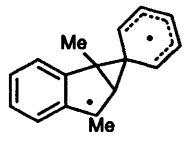
Calculations at the *ab initio* level[11] show the LUMO to be much lower in nitroethylene than in acrolein (30 and 60 kcal mol^{-1} respectively). Comparison of Table entries (iii) and (ix) shows the *E*-nitrovinyl and *E*-formylvinyl groups migrate at very similar rates. Migration of the *E*-nitrovinyl group is associated with a slightly larger solvent-rate effect (× 6 in going from Ph_2O to Me_2SO) than *E*-formylvinyl rearrangement (× 2.4). The activation entropy for a nitrovinyl shift (− 18.53 e.u.) is more negative than for a formylvinyl shift (− 12.6 e.u.). These effects suggest a more polar TS (compared to the ground state) with a more organised solvent sheath in the case of the nitroalkene.

A low π* energy in α-diketones is indicated by the long wavelength of their n-π* absorption band, *e.g.* 420 nm in biacetyl compared with 277 nm in butan-2-one. The PhCOCO group would, therefore, be expected to be a very good migrator. Comparison of entries (v) and (x) in Table 2 supports this view, the PhCOCO group migrates *ca.* 40 times faster than the benzoyl group.

ab initio Calculations show thioformaldehyde to have a lower π* energy (0.2174 a.u.) than formaldehyde (0.2815 a.u.).[13] In an attempt to test migratory aptitude for a thermally robust thiocarbonyl compound we prepared the thioamide **1** [X = C(S)NMe$_2$]. However, this compound failed to racemise at 225 °C and underwent random thermal decomposition at 230 °C. Rearrangement of **1** [X = C(S)NMe$_2$] cannot, therefore, be much faster (and could even be slower!) than for **1** [X = C(O)NMe$_2$] which rearranges cleanly at 255 °C.

Thus, for most of the entries of Table 2 the π* energy provides a fair guide to relative migratory aptitude. However, the differences in migratory aptitude that are observed are small in comparison with the changes in π* energy probably indicating other factors are also important in determining migratory aptitude.

Rearrangement of Aromatic and Heteroaromatic Groups.—Although 1,5-phenyl migration is usually preferred to alkyl migration phenyl groups actually migrate more slowly than most unsaturated groups. Thus, the aromatic group shifts in Table 3 occur much more slowly than vinyl migration [entry (vi), Table 2]. This argues against the biradical TS's of type **6** for these rearrangements proposed by others;[3,10,14] the biradical TS **17** for phenyl migration and that **18** for migration of the heterocyclic rings (X = O, S, or NPr) should be more stable than that **6** (X = CH$_2$) for vinyl migration. The very similar rearrangement rates of the 1- and 2-naphthyl groups is also inconsistent with TS's **19** and **20** of biradical type; the greater



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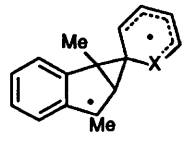

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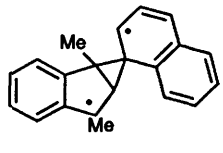

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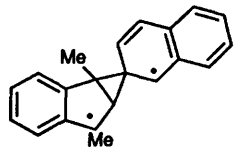

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stability of **19** should be reflected in the faster rearrangement of the 1-naphthyl group as is observed in certain photochemical reactions proceeding *via* biradical intermediates.[15] Since the more weakly aromatic heterocyclic rings migrate with greater difficulty than phenyl and naphthyl groups, loss of aromatic conjugation at the TS does not appear to be a predominating factor. Localisation energies[16] which should quantitatively

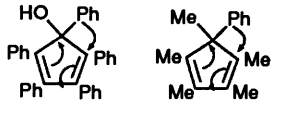
Table 3 Rate data for rearrangement of aromatic and heteroaromatic groups

Indene **1** X =	$10^5 k/s^{-1}$ (T/°C)	Localisation energy (e/V)	Method[a]/Notes
(i) 1-Naphthyl	21.8 ± 0.36 (325)	2.956	NMR
(ii) 2-Naphthyl	27.00 ± 0.28 (325)	3.162	NMR
(iii) 2-Furyl	2.12 ± 0.13 (320)	2.564	NMR
(iv) 2-Thienyl	3.62 ± 0.32 (320)	2.414	NMR
(v) 1-Propylpyrrol-2-yl	0.64 (320)	2.428	P_1
(vi) 1-Methyl-1-phenylindene	8.0 (300)	3.174	Ref. 10
(vii) 2-Pyridyl	2.94 (286)	3.155	NMR

[a] See footnote to Table 1.

reflect the stability of the radical formed as well as the aromaticity loss of migrating groups were computed by the method of Dewar (Dewar pi)[17] and are given in Table 3. These energies represent the conjugation energy lost, *e.g.* in going from benzene to a pentadienyl radical [entry (vi)]. Clearly there are greater losses associated with phenyl, 1- and 2-naphthyl, and pyridyl groups than for the 5-membered ring heterocycles. The smaller energy loss for 1-naphthyl than 2-naphthyl [entries (i) and (ii)] reflects the greater stability of the phenylpropenyl radical unit in **19** over the 2-vinylbenzyl radical moiety in **20**. The assumption of biradical TS's in which there is extensive loss of aromaticity is inconsistent with the migratory aptitudes detailed in Table 3; the smaller losses in conjugation energy predicted for the 5-membered heterocycles does not agree with their slow rearrangement compared to phenyl and naphthyl groups. Similarly, the 2-naphthyl group migrates slightly more quickly, rather than more slowly, than the 1-naphthyl group despite its predicted greater localisation energy.

ab initio Calculations (restricted Hartree–Fock with a minimal STO-3G basis set)[18] provide the following order of increasing LUMO energy: naphthalene < pyridine < thiophene ~ benzene < furan < pyrrole. Whilst this order may explain the slow migration of the 5-membered heterocycles and the fast migration of the 2-pyridyl group it fails to account for the slow shift of 1- and 2-naphthyl groups. We cannot at present propose a wholly satisfactory explanation for the data of Table 3. However, it should be noted that the differences in migratory aptitude for the aromatic groups are small and that the rate for phenyl migration refers to the 1-methylindene rather than the 1,3-dimethylindene framework; this value was also determined in another laboratory.[10] Literature data for other aryl shifts present some puzzling features. Thus phenyl shift in 1,1-diphenylindene and 1,1,3-triphenylindene is associated with large negative activation entropies (*ca.* −25 e.u.),[10] which were explained in terms of specific orientation for a bridging phenyl, as *e.g.* in **17**, together with polar solvation. However, for the phenyl shift depicted in **21** and related rearrangement of *para*-substituted phenyl groups $\Delta S^{\ddagger}$ values range from 0.2 to −12 e.u.[19] and for that in **22** $\Delta S^{\ddagger} = -6.0 \pm 0.6$ e.u.[20] A specific orientation for the bridging aryl could account for rearrangement of **23** at a temperature some 100 °C lower than required for 1-methyl-3-phenylindene;[21] **23** is set up for homoconjugative



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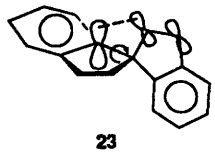

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interaction between the indene and aryl moieties so the aryl is already well orientated for rearrangement involving orbital overlap as shown in **23**; $\Delta S^{\ddagger}$ does not appear to have been obtained for this reaction. Homoconjugative effects may also explain the Woodward–Hoffmann forbidden photochemically induced 1,5-aryl shifts in indenes[22] as well as thermal rearrangement in indene dianions.[21]

Conclusions.—Several observations in the present study argue the importance of conjugative electron-withdrawal (low π^* energy) in determining the migratory aptidude of different groups, *e.g.* the fast migration of HC=CHNO$_2$, COCOPh, CO(S)Ph and the observation of HC=NBu^t and HC=NPh migration at a rate between the rates of HCO and HC=CH$_2$ rearrangement. As expected[1a] however, steric (conformational) and other orbital interaction effects can be influential and for aromatic groups this may be the case; the slow migration of the 1- and 2-naphthyl groups does not agree with the low π^* orbital energy of naphthalene. For the aromatic groups as well as others homoconjugative effects may be important and there is a need for study of more fixed models related to **23**. Good $\Delta S^{\ddagger}$ values are also required but for the high temperature reactions of Table 3 these are not easily got. Finally, the present results provide further evidence against the intervention of biradical TS's or intermediates in these rearrangements.[1e]

Experimental

For general comments see ref. 1*e*. Proton–proton coupling constants are in Hz. Polarimetric kinetic measurements were performed by dissolving 5–30 mg of the compound in diphenyl ether (*ca.* 2 cm^3), measuring the optical rotation of the solution at 37 °C (to prevent solidification of Ph_2O), recovering the solution and heating it in a long necked tube (under a slow stream of argon) placed in a Grant constant temperature bath (±0.25 °C). At regular time intervals the tube was removed from the bath, cooled and the optical rotation remeasured; the latter are recorded in units of 10^{-1} deg cm^2 g^{-1}. Kinetic runs normally continued beyond 50% racemisation and at each determination of rotation the mixture was examined by TLC to observe any random thermal decomposition.

Measurement of rearrangement rates by NMR measurements was carried out as follows. Between 2 and 30 mg of the compound was dissolved in dry C_6D_6 (0.2–0.5 cm^3) and the solution introduced into a small bore Pyrex tube that fitted snugly inside the usual NMR tube. The tubes used had been previously soaked in 2 mol dm^{-3} aqueous potassium hydroxide for at least 24 h and then washed and dried. The filled tube was sealed under vacuum after degassing of the solvent (5 freeze–pump–thaw cycles). After sealing, the tube was heated in a Grant constant temperature bath (< 250 °C) or in a fluidized sand bath (> 250 °C). At regular time intervals the tube was removed from the bath and a ^{1}H NMR spectrum obtained on a JEOL FX90Q instrument. These thermolyses were normally run to > 50% reaction.

One-point polarimetric rate constants were obtained in similar fashion but after being heated in a sealed tube the product was isolated and, if possible, purified by an appropriate means prior to measurement of the optical rotation.

(+)-1,3-*Dimethyl*-1-(E),(E)-*penta*-1,3-*dienylindene* **1** (X = E,E-*Penta*-1,3-*dienyl*).—Butyllithium (1.6 mol dm^{-3} in hexane; 0.36 cm^3, 0.58 mmol) was added dropwise to a solution of (*E*)-but-2-enyldiphenylphosphine oxide (146 mg, 0.57 mmol) in tetrahydrofuran (3 cm^3) at −78 °C. After 30 min, (+)-1,3-dimethylindene-1-carbaldehyde (100 mg, 0.58 mmol) in tetrahydrofuran (1.2 cm^3) was rapidly added. The mixture was stirred at −78 °C for 90 min and −30 °C for 45 min and then warmed to room temperature. This solution was poured into ether and washed consecutively with 1 mol dm^{-3} hydrochloric acid (×3), 1 mol dm^{-3} aqueous sodium hydrogen carbonate (×3) and water (×3). The ether layer was dried ($MgSO_4$) and evaporated to an oil. Chromatography of this on silica with light petroleum (b.p. 60–80 °C) as eluent gave the title compound as an oil (21 mg, 18%); $[\alpha]_D^{23}$ +129 (*c* 1.1 in $CHCl_3$) (Found: M^+, 210.141. $C_{16}H_{18}$ requires: *M*, 210.141); ν_{max}(film)/cm^{-1} 1610, 1450, 1385, 990, 820 and 755; δ_H(400 MHz), 7.23 (4 H, m, ArH), 6.15 (1 H, dd, *J* 15.5 and 10), 6.00 (2 H, m), 5.89 (1 H, q, *J* 2), 5.61 (1 H, dq, *J* 14 and 7), 5.51 (1 H, d, *J* 15.5), 2.11 (3 H, d, *J* 2), 1.72 (3 H, dd, *J* 7 and 2) and 1.39 (3 H, s); *m/z* 210, 195, 180, 165, 152, 141, 128, 115, 89 and 77 (83.0, 100.0, 46.5, 53.9, 13.2, 16.0, 23.8, 17.3, 21.5 and 9.4%).

(+)-1,3-*Dimethyl*-1-(E)-*nitrovinylindene*.—Potassium fluoride (1.7 mg, 0.03 mmol) and nitromethane (63 mm^3, 12 mmol) were added to a solution of (+)-1,3-dimethylindene-1-carbaldehyde (100 mg, 0.58 mmol) in isopropyl alcohol (0.6 cm^3). After 6.5 h 18-crown-6 (7.7 mg, 0.03 mmol) in isopropyl alcohol (0.1 cm^3) was added, and after 29 h further potassium fluoride (1.7 mg, 0.03 mmol) was added. After 71 h the solution was diluted with ether and poured into water. The layers were separated and the aqueous layer extracted with ether (×3). Drying ($MgSO_4$) and evaporation of the combined extracts gave an oil (72 mg). Without further purification the oil was dissolved in dichloromethane (2 cm^3) and the resulting solution cooled to 0 °C. Methanesulfonyl chloride (24 mm^3, 0.31 mmol) was rapidly syringed into the mixture, and then triethylamine (86 mm^3, 0.62 mmol) was added dropwise. After 2 h the solution was warmed to room temperature and diluted with dichloromethane. The mixture was washed with water (×2), 1 mol dm^{-3} hydrochloric acid (×2) and brine (×2). Drying ($MgSO_4$) of the organic layer and evaporation gave an oil (62 mg). Chromatography of the latter on silica in benzene gave (+)-1,3-dimethyl-1-(*E*)-nitrovinylindene as an oil (26 mg, 21%) $[\alpha]_D^{21}$ +221 (*c* 0.98 in $CHCl_3$) (Found: M^+, 215.095. $C_{13}H_{13}NO_2$ requires *M*, 215.095); λ_{max}/nm 249 and 309 (ε/dm^3 mol^{-1} cm^{-1} 142 256 and 2938); ν_{max}(film)/cm^{-1} 1640, 1525 and 1355; δ_H(400 MHz) 7.32 (4 H, m, ArH), 7.14 (1 H, d, *J* 13.5), 7.06 (1 H, d, *J* 13.5), 5.97 (1 H, q, *J* 2), 2.16 (3 H, d, *J* 2) and 1.50 (3 H, s); *m/z* 215, 198, 180, 153, 146, 128, 115, 77, 63 and 51 (63, 57, 34, 84, 100, 99, 62, 25, 25 and 27%).

1,3-*Dimethyl*-2-(E)-*nitrovinylindene*.—A solution of (+)-1,3-dimethyl-1-(*E*)-nitrovinylindene (9 gm, 0.04 mmol) in deuteriobenzene (0.4 cm^3) was degassed in a small bore tube and the tube sealed under vacuum. The tube was heated for 3.5 h at 170 °C and then opened and the contents chromatographed on silica with benzene to give the title compound (3 mg, 33%); m.p. 98–100 °C (from light petroleum) (Found: M^+, 215.094. $C_{13}H_{13}NO_2$ requires *M*, 215.095); ν_{max}(Nujol)/cm^{-1} 1610 and 1330; δ_H(400 MHz) 8.18 (1 H, d, *J* 13.5), 7.43 (4 H, m, ArH), 7.26 (1 H, d, *J* 13.5), 3.60 (1 H, qq, *J* 7.5 and 2), 2.39 (3 H, d, *J* 2) and 1.38 (3 H, d, *J* 7.5); *m/z* 215, 198, 180, 152, 146, 128, 115, 76, 69 and 51 (75, 50, 98, 100, 61, 54, 36, 30 and 30%).

Preparation of 2-(1,3-*Dimethylinden*-1-*ylcarbonyl*)-2-*phenyl*-1,3-*dithiane* **7**.—Butyllithium (1.6 mol dm^{-3} hexane; 0.72 cm^3, 1.16 mmol) was added dropwise to a solution of 2-phenyl-1,3-dithiane (208 mg, 1.06 mmol) in tetrahydrofuran (5 cm^3) at −40 °C. The mixture was stirred for 4 h at −25 and −15 °C, and then a portion of the solution (2.5 cm^3) was added dropwise to a solution of 1-chloroformyl-1,3-dimethylindene (129 mg; crude) in tetrahydrofuran (5 cm^3) at −76 °C. This mixture was warmed to room temperature, stirred for 18 h and then diluted with water. The aqueous solution was extracted with ether (×3) and the combined organic phases were washed with 1 mol dm^{-3} aqueous hydrogen carbonate (×3), water (×2) and brine (×2). Drying ($MgSO_4$) and evaporation gave an oil (165 mg), which was chromatographed on silica with petroleum–benzene (7:3) to give the title compound **7** as a solid (84 mg, 35%), m.p. 108–110 °C (from pentane); $[\alpha]_D^{24}$ +258 (*c* 0.72 in $CHCl_3$) (Found: C, 72.1; H, 6.0; S, 17.5%; M^+, 366.110. $C_{22}H_{22}S_2O$ requires: C, 72.1; H, 6.05; S, 17.5%; *M*, 366.111); ν_{max}(Nujol)/cm^{-1} 1685; δ_H 90 MHz) 7.70 (1 H, m), 7.10 (8 H, m, ArH), 5.70 (1 H, q, *J* 2), 3.5 to 1.7 (6 H, m), 1.65 (3 H, d, *J* 2) and 1.55 (3 H, s); *m/z* 366, 217. 195, 143, 128, 121, 91, 77, 69 and 45 (0.6, 1.5, 100.0, 7.8, 14.6, 24.4, 1.6, 4.6, 3.0 and 1.4%).

Preparation of 1-*Benzoylcarbonyl*-1,3-*dimethylindene* **1** (X = COCOPh).—The dithiane **7** (43.2 mg, 0.12 mmol) in acetonitrile (1.5 cm^3) was added to a stirred solution of *N*-chlorosuccimide (64 mg, 0.48 mmol), silver nitrate (92 mg, 0.54 mmol) and 2,4,5-trimethylpyridine (174 mg, 1.44 mmol) in acetonitrile–water (8:2) (5 cm^3). After 30 min the mixture was shaken with saturated aqueous sodium thiosulfate, saturated aqueous sodium carbonate and brine, filtered, diluted with dichloromethane–hexane (1:1), dried ($MgSO_4$) and evaporated. The oily residue was dissolved in ether and the solution washed with 1 mol dm^{-3} hydrochloric acid, 1 mol dm^{-3} aqueous sodium hydrogen carbonate, water and brine, dried ($MgSO_4$) and evaporated to give an oil (20 mg). Chromatography of the latter on silica with benzene–light petroleum (1:1) gave **1** (X = COCOPh) as an oil (13 mg, 39%); $[\alpha]_D^{24}$ +220 (*c* 0.66 in $CHCl_3$) (Found: M^+, 276.114. $C_{19}H_{16}O_2$ requires *M*, 276.115); ν_{max}(film)/cm^{-1} 1695 and 1670; δ_H(90 MHz) 7.35 (9 H, m, ArH), 6.15 (1 H, q, *J* 2), 2.10 (3 H, d, *J* 2) and 1.70 (3 H, s); *m/z* 276, 143, 128, 105, 77 and 57 (3.1, 10.8, 13.1, 100.0, 22.5 and 12.0%).

(+)-*Phenyl* 1,3-*Dimethylindene*-1-*thiocarboxylate*.—Thiophenol (110 mm^3, 1.07 mmol) was added to a solution of (+)-1,3-dimethylindene-1-carboxylic acid (100 mg, 0.53 mmol) in 1,2-dimethoxyethane (2.65 cm^3). The solution was cooled to 0 °C and then treated with pyridine (130 mm^3, 1.6 mmol) and phenyl dichlorophosphate (120 mm^3, 0.8 mmol). The mixture was stirred at room temperature for 16 h and then poured into ice cold 1 mol dm^{-3} aqueous sodium hydroxide. This solution was extracted with chloroform (×3) and the extracts were washed with 1 mol dm^{-3} aqueous sodium hydroxide (×2) and brine (×2), dried ($MgSO_4$), and evaporated to give an oil (150 mg). Chromatography of the latter on silica with benzene–light petroleum (6:4) gave the title compound **1** (X = COSPh) as an oil (116 mg, 77%); $[\alpha]_D^{24}$ +11 (*c* 1.1 in $CHCl_3$); $[\alpha]_D^{37}$ −47 (*c* 1.05 in Ph_2O) (Found: M^+, 280.092. $C_{18}H_{16}OS$ requires: *M*, 280.092; ν_{max}(Nujol)/cm^{-1} 1695; δ_H(400 MHz) 7.37 (9 H, m, ArH), 6.23 (1 H, q, *J* 1.5), 2.27 (3 H, d, *J* 1.5) and 1.61 (3 H, s); *m/z* 280, 143, 128, 115, 109, 91, 77, 71, 65 and 51 (5, 100, 38, 11, 8, 3, 5, 2, 7 and 6%).

Phenyl 1,3-*Dimethylindene*-2-*thiocarboxylate*.—(+)-Phenyl 1,3-dimethylindene-1-thiocarboxylate (21 mg, 0.08 mmol) dissolved in diphenyl ether (2 cm^3) and the solution heated at 190 °C for *ca.* 20 h. Chromatography on silica with light petroleum–benzene (70:30) gave phenyl-1,3-dimethylindene-1-thiocarboxylate (1 mg, 5%) followed by the title compound (7 mg, 31%) (Found: M^+, 280.092. $C_{18}H_{16}OS$ requires *M*, 280.092); ν_{max}(Nujol)/cm^{-1} 1650, 1320, 1210, 1150, 865 and

745; δ_H(90 MHz) 7.46 (9 H, m, ArH), 3.94 (1 H, qq, *J* 7.7 and 2.6), 2.54 (3 H, d, *J* 2.6), and 1.56 (3 H, d, *J* 7.7); *m/z* 280, 171, 156, 143, 128, 115 and 65 (0.3, 100.0, 6.2, 5.1, 25.6, 7.1 and 5.0%).

Preparation of 1,3-*Dimethyl*-1-(N,N-*dimethylaminocarbonyl*)-*indene* **1** (X = $CONMe_2$).—(+)-1,3-Dimethylindene-1-carboxylic acid (376 mg, 2 mmol) was held at 0 °C and oxalyl chloride (7.5 cm^3) added to it. After 4 h at room temperature the solution was evaporated and the residue taken up in benzene and evaporated three times. The residue was dissolved in ether and dimethylamine gas passed through the solution for 20 min. After a further 30 min the solution was washed with water, dried ($MgSO_4$) and evaporated to give the title compound **1** (X = $CONMe_2$) as a solid (415 mg, 97%); m.p. 81–83 °C; $[\alpha]_D^{24}$ + 86 (*c* 1.20 in $CHCl_3$) (Found: M^+, 215.131. $C_{14}H_{17}NO$ requires *M*, 215.131; ν_{max}(Nujol)/cm^{-1} 1640, 1260, 1160, 1060, 830 and 775 cm^{-1}; δ_H(90 MHz) 7.30 (4 H, m, ArH), 6.15 (1 H, q, *J* 2), 2.50 (6 H, br s), 2.15 (3 H, d, *J* 2) and 1.45 (3 H, s); *m/z* 215, 143, 128, 115 and 72 (7.5, 10.5, 13.9, 6.1 and 100.0%).

Preparation of 1,3-*Dimethyl*-2-(NN-*dimethylaminocarbonyl*)-*indene* **3** (X = $CONMe_2$).—A solution of the foregoing dimethylamide (24 mg, 0.11 mmol) in diphenyl ether (2 cm^3) was heated at 255 °C for *ca.* 18 h. Chromatography on silica with ether gave the title compound **3** (X = $CONMe_2$) as an oil (13 mg, 53%); (Found: M^+, 215.131. $C_{14}H_{17}NO$ requires *M*, 215.131); ν_{max}(film)/cm^{-1} 2940, 1670, 1630, 1500, 1450, 1400 and 770; δ_H(90 MHz) 7.30 (4 H, m, ArH), 4.85 (1 H, qq, *J* 8 and 2), 3.08 (6 H, br d), 2.10 (3 H, d, *J* 2) and 1.35 (3 H, d, *J* 8); *m/z* 215, 171, 156, 141, 128, 115 and 72 (21.8, 48.2, 5.8, 11.7, 27.1, 13.4 and 100.0%).

Preparation of 1,3-*Dimethyl*-1-(N,N-*dimethylaminothiocarbonyl*)*indene* **1** (X = $CSNMe_2$).—Lawessons's reagent (188 mg, 0.5 mmol) was added to a solution of the dimethylamide **1** (X = $CONMe_2$) (100 mg, 0.5 mmol) in toluene (2 cm^3), and the resulting mixture refluxed for 4 h. After cooling the solution was chromatographed on silica with light petroleum and then with light petroleum–ethyl acetate (85:15) to give the title compound **1** (X = $CSNMe_2$) as an oil which solidified with time (90 mg, 78%); m.p. 101–102 °C (from ether–hexane); $[\alpha]_D^{24}$ +35 (*c* 2.5 in $CHCl_3$) (Found: C, 72.65; H, 7.4; N, 5.95; S, 13.9%; M^+, 231.108. $C_{14}H_{17}NS$ requires C, 72.7; H, 7.4; N, 6.1; S, 13.8%; *M*, 231.108); ν_{max}(film)/cm^{-1} 1490, 1360, 1040, 800 and 760; δ_H(90 MHz) 7.29 (4 H, m, ArH), 6.19 (1 H, q, *J* 2), 3.42 (3 H, br s), 2.45 (3 H, br s), 2.15 (3 H, d, *J* 2) and 1.70 (3 H, s); *m/z* 231, 141, 128, 88 and 72 (12.8, 6.1, 11.0, 100.0 and 5.2%).

Attempted Rearrangement of the Dimethylthioamide **1** (X = $CSNMe_2$).—(*a*) A solution of the dimethylthioamide **1** (X = $CSNMe_2$) (10.6 mg, 0.05 mmol) in deuteriobenzene (*ca.* 0.4 cm^3) was degassed in a small bore tube and the tube sealed under vacuum. Heating of the tube < 225 °C caused no reaction observable by NMR. However, when the tube was heated at 255 °C for 15 min degradation of the dimethylthioamide was observed by NMR.

(*b*) A solution of the dimethylthioamide (50 mg, 0.23 mmol; previously purified by recrystallization) in diphenyl ether (2 cm^3) was heated at 175 °C for 91 min. Chromatography on silica with hexane–ether (9:1) gave recovery of dimethylthioamide as an oil (39 mg, 78%); $[\alpha]_D^{24}$ +35 (*c* 1.95 in $CHCl_3$). Pure material also has $[\alpha]_D^{24}$ +35.

Preparation of the 1-(tert-*Butyliminomethyl*)-1,3-*dimethylindene.* **1** (X = HC=NBu^t).—(+)-1,3-Dimethylindene-1-carbaldehyde (100 mg, 0.58 mmol) and *tert*-butylamine (127 mg, 1.74 mmol) were dissolved in dichloromethane (6 cm^3), and the mixture stirred with type 4A molecular sieves (*ca.* 3 g) for 16 h. Removal of the sieves and evaporation gave an oil (90 mg), which was distilled (101–106 °C/0.01 mmHg) to give the title compound (87 mg, 66%); $[\alpha]_D^{24}$ +72 (*c* 1.08 in C_6D_6) (Found: M^+, 227.168. $C_{16}H_{21}N$ requires *M*, 227.167); ν_{max}(film)/cm^{-1} 1650, 1450 and 1365; δ_H(400 MHz; C_6D_6) 7.28 (4 H, m, ArH), 6.97 (1 H, s), 6.00 (1 H, q, *J* 1.5), 2.17 (3 H, d, *J* 1.5), 1.45 (3 H, s) and 1.14 (9 H, s); *m/z* 227, 172, 144, 128, 115, 91, 84, 77, 63 and 57 (2, 2, 46, 20, 7, 1, 4, 2, 2 and 100%).

The following imines were prepared using the same method.

(a) *The anil* **1** (X = HCNPh) *of* (+)-1,3-*dimethylindene*-1-*carbaldehyde.* Distilled (144–147 °C/0.01 mmHg) as an oil (77 mg, 53%); $[\alpha]_D^{24}$ +264 (*c* 1.0 in C_6H_6) (Found: M^+, 247.136. $C_{18}H_{17}N$ requires *M*, 247.136); ν_{max}(film)/cm^{-1} 1630; δ_H(400 MHz; C_6D_6) 7.10 (10 H, m, ArH and imine H), 5.84 (1 H, q, *J* 1.5), 1.91 (3 H, d, *J* 1.5) and 1.72 (3 H, s); *m/z* 247, 172, 144, 129, 115, 104, 93, 77, 65 and 51 (8, 4, 100, 59, 20, 81, 13, 64, 8 and 18%).

(b) *The anil* **3** (X = HCNPh) *of* 1,3-*dimethylindene*-2-*carbaldehyde.* Removal of the sieves and evaporation gave an oil, which was dissolved in benzene, evaporated and heated under vacuum three times to give the anil as an oil (83%) (Found: M^+, 247.136. $C_{18}H_{17}N$ requires *M*, 247.136); ν_{max}(film)/cm^{-1} 1580; δ_H(400 MHz; C_6D_6) 8.46 (1 H, s), 7.19 (9 H, m, ArH), 4.01 (1 H, dq, *J* 2 and 7.5), 1.94 (3 H, d, *J* 2), and 1.66 (3 H, d, *J* 7.5); *m/z* 247, 232, 217, 144, 128, 115, 104, 93, 77 and 51 (37, 32, 8, 15, 20, 12, 55, 32, 100 and 42%).

(c) *Deuteroanil* **1** (X = DCNPh). Distillation (144–148 °C at 0.01 mmHg) gave the deuterioanil (62%); $[\alpha]_D^{24}$ +224 (*c* 0.97 in C_6H_6) (Found: M+, 248.142. $C_{18}H_{16}ND$ requires *M*, 248.142); ν_{max}(film)/cm^{-1} 1580; δ_H(400 MHz; C_6D_6) 7.00 (9 H, m, aromatic), 5.84 (1 H, q, *J* 2), 1.91 (3 H, d, *J* 2) and 1.72 (3 H, s); *m/z* 248, 173, 145, 130, 115, 105, 94, 77, 63, and 51 (10, 3, 80, 46, 21, 100, 9, 87, 8 and 34%).

(d) *Deuterioanil* **3** (X = DCNPh). Distilled (170 °C/0.01 mmHg) as an oil (108 mg, 76%) (Found: M^+, 248.142. $C_{18}H_{16}ND$ requires *M*, 248.142); ν_{max}(film)/cm^{-1} 1610, 1570, 1210, 760, 725 and 700; δ_H(90 MHz; C_6D_6) 7.25 (9 H, m, ArH), 4.10 (1 H, qd, *J* 6 and 2), 2.05 (3 H, d, *J* 2) and 1.75 (3 H, d, *J* 6); *m/z* 248, 233, 218, 156, 145, 128, 105, 91, 77 and 51 (89.0, 76.2, 10.7, 10.4, 23.0, 20.4, 79.6, 6.3, 100.0 and 24.3%).

The anil **3** (X = HCNPh) *of* 1,3-*dimethylindene*-2-*carbaldehyde.* A solution of the phenyl imine **1** (X = HCNPh) (19.9 mg, 0.08 mmol) in deuteriobenzene (0.4 cm^3) was degassed in a small bore tube sealed under vacuum. The tube was heated at 170 °C for 22 h, to give the anil (95% by NMR) and 1,3-dimethylindene-2-carbaldehyde (5% by NMR).

1,3-*Dimethylindene*-2-[^{2}H]*carbaldehyde***3**(X = CDO).—1,3-Dimethylindene-1-[^{2}H]carbaldehyde **1** (X = CDO) (198 mg, 1.14 mmol) was dissolved in pyridine (15 cm^3) and the solution refluxed for 22 h. The cooled solution was evaporated to give a brown oil, which was dissolved in ether and washed with 1 mol dm^{-3} hydrochloric acid, 1 mol dm^{-3} aqueous sodium hydrogen carbonate and brine. Drying ($MgSO_4$) and evaporation gave an oil (188 mg). Chromatography on silica in benzene–ether (99:1) gave the title compound **3** (X = CDO) as an oil (178 mg, 90%) (Found: M^+, 173.095. $C_{12}H_{11}DO$ requires *M*, 173.095); ν_{max}(Nujol)/cm^{-1} 2920, 2100, 1630, 1460, 1385 and 1355; δ_H(90 MHz) 7.25 (4 H, m, ArH), 3.55 (1 H, qd, *J* 6 and 2), 2.35 (3 H, d, *J* 2) and 1.25 (3 H, d, *J* 6); *m/z* 173, 145, 130, 115, 102, 77, 63 and 51 (35, 64, 100, 21, 6, 11, 10 and 13%).

Cross-over Experiment.—A solution of 1,3-dimethylindene-1-[^{2}H]carbaldehyde (50.6 mg, 0.3 mmol) and the phenylimine **1** (X = HCNPh) (72.9 mg, 0.3 mmol) in dry benzene (*ca.* 0.4 cm^3) containing one drop of deuterioacetonitrile was degassed in a small bore tube, and the tube sealed under vacuum. The tube was heated at 170 °C for 260 min after which the relative amounts of deuterioaldehydes [1,3-dimethylindene-1-[^{2}H]car-

baldehyde **1** (X = CDO) and 1,3-dimethyl indene-2-[^{2}H]carbaldehyde **3** (X = CDO) and deuterioanils **1** (X = DCNPh) and **3** (X = DCNPh)] determined by ^{2}H NMR (34, 27, 18 and 22% respectively). This gave a single-point exchange rate of 3.17×10^{-5} s^{-1}. The original imine rearrangements contained *ca.* 10% or less of 1,3-dimethylindene-1-carbaldehyde, so that the exchange rate would be *ca.* 0.63×10^{-5} s^{-1}. The deuterium NMR signals for the compounds involved in this experiment were measured (400 MHz) in C_6H_6 in the presence of a trace of CD_3CN and appeared as follows relative to CD_3CN and C_6D_6: **1** (X = CDO); δ_D = 8.45; **3** (X = CDO); δ_D = 10.15; **3** (X = DCNPh), δ_D = 8.58; **1** (X = DCNPh), δ_D = 7.25.

The Dimethylhydrazone **1** (X = HCNNMe$_2$).—(+)-1,3-Dimethylindene-1-carbaldehyde (100 mg, 0.58 mmol), 1,1-dimethylhydrazine (105 mg, 1.75 mmol) and glacial acetic acid (0.2 cm^3) were dissolved in ethanol (2 cm^3). The mixture was stirred at room temperature for 75 min and then diluted with chloroform. The solution was washed consecutively with 1 mol dm^{-3} aqueous sodium hydrogen carbonate (×2), water (×2) and brine (×2). Drying ($MgSO_4$) and evaporation gave an oil (96 mg). Chromatography on silica with benzene–ether (95:5) gave **1** (X = HCNNMe$_2$) as an oil (83 mg, 64%); $[\alpha]_D^{24}$ +188 (*c* 1.1 in $CHCl_3$) (Found: M$^+$, 214.147. $C_{14}H_{18}N_2$ requires *M*, 214.147); ν_{max}(film)/cm^{-1} 1465, 1440, 1015 and 755; δ_H(400 MHz) 7.26 (4 H, m, ArH), 6.25 (1 H, br s), 6.03 (1 H, q, *J* 2), 2.71 (6 H, s), 2.14 (3 H, d, *J* 2), and 1.46 (3 H, s); *m/z* 214, 199, 170, 156, 141, 128, 115, 77, 71, 51 and 44 (54.3, 15.4, 16.8, 27.1, 23.4, 38.7, 19.6, 7.1, 41.0, 8.5 and 100%).

The Dimethylhydrazone **3** (X = HCNNMe$_2$).—A solution of the foregoing dimethylhydrazone (22 mg, 0.10 mmol) in diphenyl ether (2 cm^3) was heated at 220 °C for 2.5 h. Chromatography on silica with benzene–ether (95:5) gave starting material (1 mg, 5%). Further elution gave the dimethylhydrazone **3** (X = HCNNMe$_2$) as an oil (4 mg, 20%) (Found: M$^+$, 214.147. $C_{14}H_{18}N_2$ requires *M*, 214.147); ν_{max}(film)/cm^{-1} 1730 and 1460; δ_H(90 MHz) 7.4 (1 H, s), 7.24 (4 H, m), 3.7 (1 H, qq, *J* 8 and 1), 2.9 (6 H, s), 2.2 (3 H, d, *J* 1) and 1.4 (3 H, d, *J* 8); *m/z* 214, 199, 170, 154, 141, 128, 115 and 71 (95.0, 21.2, 29.4, 50.9, 32.6, 39.5, 24.9 and 44.4%).

Preparation of 1-(4,4-*Dimethoxybutylcarbonyl*)-1-*methylindene* **8** [X = O, X^1 = (OMe)$_2$].—A solution of 1-bromo-4,4-dimethoxybutane (1.5 g, 7.7 mmol) in tetrahydrofuran (6 cm^3) was syringed onto magnesium turnings (179 mg, 7.5 mmol) and the mixture heated at 40 °C for 190 min. The solution was cooled to 0 °C and (+)-1,3-dimethylindene-1-carbaldehyde (975 mg, 5.7 mmol) in tetrahydrofuran (1.8 cm^3) syringed into the solution. After 105 min at 0 °C the mixture was poured into ice cold water and extracted with ether. The extract was washed with 1 mol dm^{-3} aqueous sodium carbonate, dried ($MgSO_4$) and evaporated to give the expected alcohol as an oil (1.59 g); ν_{max}(film)/cm^{-1} 3480, 2940, 1450 and 1350; δ_H(90 MHz) 7.25 (4 H, m, ArH), 6.10 (1 H, m), 4.30 (1 H, m), 3.50 (7 H, m), 2.10 (3 H, s) and 1.50 (9 H, m).

Chromium trioxide (3.85 g, 38.5 mmol) was rapidly added to a solution of pyridine (6.08 g, 77 mmol) in dichloromethane (150 cm^3) at 0 °C, and the solution stirred at room temperature for 20 min. A solution of the foregoing alcohol (crude; 1.59 g) in dichloromethane (20 cm^3) was pipetted into the mixture and the resulting solution stirred for 70 min. Ether was then added and the mixture washed consecutively with 2 mol dm^{-3} aqueous sodium carbonate, 0.1 mol dm^{-3} hydrochloric acid, 1 mol dm^{-3} aqueous sodium hydrogen carbonate and brine. Drying ($MgSO_4$) and evaporation gave an oil which was chromatographed on silica with benzene–ether (9:1) to give the title compound as an oil (833 mg, 51%); $[\alpha]_D^{24}$ +114 (*c* 1.29 in $CHCl_3$); ν_{max}(film)/cm^{-1} 2920, 1700 and 1120; δ_H(90 MHz) 7.30 (4 H, m, ArH), 6.03 (1 H, q, *J* 2), 4.15 (1 H, t, *J* 5), 3.20 (6 H, s), 2.20 (3 H, d, *J* 2), 1.90 (2 H, m) and 1.35 (7 H, m); *m/z* 256, 185, 143, 128, 113, 99, 85, 75, 71 and 55 (5.1, 2.5, 11.5, 13.5, 22.7, 2.9, 5.3, 6.2, 100.0 and 14.8%).

1-(1,5-*Dihydroximinopentyl*)-1-*methylindene* **8** (X = X^1 = NOH).—The ketone **8** [X = O; X^1 = (OMe)$_2$] (350 mg, 1.2 mmol) and pyridine (517 mg, 6.5 mmol) were dissolved in chloroform–ethanol (1:1); 14 cm^3) and added to a solution of hydroxylamine hydrochloride (455 mg, 6.5 mmol) in ethanol–water (5:1; 8.4 cm^3). The resulting solution was refluxed for 4 h, poured into ether and washed with 0.1 mol dm^{-3} hydrochloric acid and water. Drying ($MgSO_4$) and evaporation gave an oily residue, which was chromatographed on silica with benzene–ether (9:1) to provide the title compound **8** (X = X^1 = NOH) as a clear oil (311 mg, 95%); $[\alpha]_D^{24}$ +34 (*c* 1.69 in $CHCl_3$) (Found: M$^+$, 272.152. $C_{16}H_{20}N_2O_2$ requires *M*, 272.152); ν_{max}(CH_2Cl_2)/cm^{-1} 3560, 3280br and 940; δ_H(90 MHz) 9.00 (2 H, br s), 7.30 (4 H, m, ArH), 6.40 (1 H, t, *J* 5), 5.95 (1 H, q, *J* 2), 2.25 (3 H, d, *J* 2), 1.95 (2 H, m), 1.60 (4 H, m), and 1.40 (3 H, s); *m/z* 272, 243, 194, 182, 169, 160, 143, 128, 115 and 86 (13.7, 23.6, 18.7, 11.9, 19.6, 62.5, 77.2, 100.0, 31.0 and 24.7%).

(+)-1,3-*Dimethyl*-1-(2-*pyridyl*)*indene* **1** (X = 2-*pyridyl*).—A solution of the foregoing bis-oxime (311 mg, 1.14 mmol) in benzene was refluxed for 50 min while hydrogen chloride gas was bubbled rapidly through the mixture. The cooled solution was poured into 1 mol dm^{-3} aqueous sodium hydrogen carbonate and extracted with dichloromethane. The extract was washed with water, dried ($MgSO_4$), evaporated, and the residue chromatographed on silica with benzene to give the title compound as an oil (128 mg, 51%); $[\alpha]_D^{24}$ +118 (*c* 0.33 in $CHCl_3$) (Found: M$^+$, 221.120. $C_{16}H_{15}N$ requires *M*, 221.120); ν_{max}(CH_2Cl_2)/cm^{-1} 1585 and 1465; δ_H(90 MHz) 8.60 (1 H, m, ArH), 7.25 (7 H, m, ArH), 6.30 (1 H, q, *J* 2), 2.20 (3 H, d, *J* 2) and 1.80 (3 H, s); *m/z* 221, 206, 141, 128, 115, 110, 102, 84, 78 and 49 (100.0, 87.0, 12.5, 23.6, 11.2, 8.4, 8.2, 30.9, 22.5 and 56%).

1,3-*Dimethyl*-2-(2-*pyridyl*)*indene* **3** (X = 2-pyridyl).—A solution of (+)-1,3-dimethyl-1-(2-pyridyl)indene (22.4 mg, 0.10 mmol) in diphenyl ether (0.4 cm^3) was degassed in a small bore tube, and the tube sealed under vacuum. The tube was heated for 4 h in a Woods metal bath at 295 °C and then cooled, opened and the contents combined with a previously prepared sample (6 mg). Chromatography on silica with benzene–ether (95:5) gave the title compound (17.4 mg) and further elution gave starting material (2.5 mg) as oils (Found: M$^+$, 221.120. $C_{16}H_{15}N$ requires *M*, 221.120); ν_{max}(film)/cm^{-1} 1575, 1455 and 740; δ_H(90 MHz) 8.70 (1 H, d, q, *J* 5 and 1), 7.30 (7 H, m, ArH), 4.10 (1 H, qq *J* 7.5 and 2), 2.40 (3 H, d, *J* 2) and 1.25 (3 H, d, *J* 7.5); *m/z* 221, 206, 191, 181, 141, 128, 115, 103, 93 and 78 (100.0, 95.0, 4.3, 7.9, 7.5, 14.0, 9.7, 17.3, 8.5 and 26.2%).

(+)-2-(1,3-*Dimethylinden*-1-*yl*)-1-*methylpyridinium Tetrafluoroborate* **10**.—A solution of (+)-1,3-dimethyl-1-(2-pyridiyl)-indene (100 mg, 0.45 mmol) in dichloroethane (0.5 cm^3) was syringed onto trimethyloxonoium tetrafluoroborate (66.9 mg, 0.45 mmol) and the mixture heated to 50 °C. The resulting solution was cooled to 0 °C and then evaporated to give a brown solid. Crystallization of this from dichloromethane–ether gave the title compound **10** as white crystals (115 mg, 79%); m.p. 189–190 °C (from dichloromethane–ether); $[\alpha]_D^{24}$ +106 (*c* 1.04 in $CHCl_3$); (Found: C, 62.9; H, 5.5; N, 4.3. $C_{17}H_{18}NBF_4$ requires C, 63.2; H, 5.6; N, 4.3%); ν_{max}(Nujol)/cm^{-1} 1620, 1510 and 1060br; δ_H(90 MHz) 8.75 (1 H, d, *J* 5), 8.55 (1 H, t d, *J* 5 and 2), 8.35 (1 H, dd, *J* 5 and 2), 7.90 (1 H, t d, *J* 5 and 2), 7.25 (4 H, m, ArH), 6.25 (1 H, q, *J* 2), 3.55 (3 H, s), 2.25 (3 H, d, *J* 2) and 1.85 (3 H, s).

Thermolysis of the Salt **10**.—(*a*) The tetrafluoroborate salt (25 mg, 0.08 mmol) in deuterioacetonitrile (*ca.* 0.4 cm^3), was degassed in a small bore tube and sealed under vacuum. The tube was heated in a constant temperature oil bath at 220 °C for 1 h and then examined by NMR. Since no change could be seen in the material heating was continued at 240 °C. Examination at 1 h intervals by NMR showed the salt to be decomposing without the formation of recognisable products.

(*b*) The salt (60 mg) in acetonitrile (*ca.* 0.4 cm^3) was sealed into a thick-walled Pyrex tube and the latter heated at 200 °C for 2 h. It was then opened and the solvent evaporated to provide the product (58 mg); $[\alpha]_D^{24}$ +103 (*c* 1.17 in $CHCl_3$). A solution of this solid (58 mg) in monoglyme (15 cm^3) was mixed with sodium iodide (135 mg, 0.9 mmol) and water (1 cm^3) and stirred for 12 h. The solvent was evaporated and the residue dissolved in chloroform, and the solution filtered. ^1H NMR spectroscopy showed that complete conversion into the iodide salt had occurred. Half the solid was mixed with toluene (25 cm^3) and chloroform (1 cm^3) and the solution refluxed for 2 h, with a fast stream of argon bubbling through the mixture. The solvent was evaporated and the residue dissolved in ether. The solution was washed with 1 mol dm^{-3} aqueous sodium thiosulfate and water, dried ($MgSO_4$) and evaporated to give an oil. Chromatography of this on silica with benzene–ether (99:1) gave (+)-1,3-dimethyl-1-(2-pyridyl)indene as an oil (15.4 mg); $[\alpha]_D^{24}$ +114 (*c.* 0.77 in $CHCl_3$).

1,3-*Dimethyl*-1-(2-*naphthyl*)*indene* **1** (X = 2-naphthyl).—Butyllithium (1.6 mol dm^{-3} solution in hexane; 1.3 cm^3, 2.1 mmol) was added dropwise to a solution of 1,3-dimethylindene (300 mg, 2.1 mmol) in tetrahydrofuran (1 cm^3) at 0 °C, and the mixture stirred for 10 min at room temperature. 2-Bromonaphthalene (435 mg, 2.1 mmol) in tetrahydrofuran (1 cm^3) was added to the solution which was then irradiated through Pyrex glass [Hanovia 125W medium-pressure lamp] for 1 h; it was then stirred for a further 2 h. The mixture was poured into water, extracted with ether and the extracts washed with water. Drying ($MgSO_4$) and evaporation of the extracts gave an oil (629 mg). Chromatography of the latter on silica with hexane gave the title compound as an oil (226 mg). Crystallization gave a white solid (179 mg, 31%); m.p. 112–115 °C (from ether–methanol) (Found: C, 93.3; H, 6.5%; M^+, 270.140. $C_{21}H_{18}$ requires C, 93.3; H, 6.7%; *M*, 270.141); ν_{max}(Nujol)/cm^{-1} 3020, 1640, 1580, 1500, 840 and 750; δ_H(90 MHz) 7.95 to 6.95 (11 H, m, ArH), 6.25 (1 H, q, *J* 2), 2.20 (3 H, d, *J* 2) and 1.78 (3 H, s); *m/z* 270, 255, 239, 142 and 126 (100.0, 74.4, 20.5, 17.0 and 19.4%).

Repetition of this experiment using 1-bromonaphthalene also gave **1** (X = 2-naphthyl) (26%). This yield increased to 46% when the mixture was allowed to stand in the dark (3 h) rather than being irradiated.

1,3-*Dimethyl*-2-(2-*naphthyl*)*indene* **3** (X = 2-naphthyl).—A solution of 1,3-dimethyl-1-(2-naphthyl)indene (12 mg, 0.04 mmol) in deuteriobenzene (0.4 cm^3) was degassed in a small bore tube and the latter then sealed under vacuum. The tube was heated at 195 °C for 18.5 h and then opened and the solvent evaporated. Chromatography of the residue on silica with petroleum–benzene (9:1) gave the title compound as an oil (9 mg, 75%) (Found: M^+, 270.141. $C_{21}H_{18}$ requires *M*, 270.141); ν_{max}(film)/cm^{-1} 1580, 1490, 900, 820 and 750; δ_H(400 MHz) 7.90 (4 H, m, ArH), 7.6–7.2 (7 H, m, ArH), 4.03 (1 H, q q, *J* 7 and 2), 2.34 (3 H, d, *J* 2) and 1.25 (3 H, d, *J* 7); *m/z* 270, 255, 239, 228, 142, 126 and 115 (100.0, 64.2, 20.4, 6.4, 12.0, 19.2 and 6.4%).

3-*Methylindenone*.—3-Methylindanone (5.3 g, 36 mmol), *N*-bromosuccinimide (6.2 g, 35 mmol) and benzoyl peroxide (50 mg) were heated on a steam-bath in carbon tetrachloride (45 cm^3) for 40 min. After the mixture had been cooled in ice the succinimide was filtered off and washed with carbon tetrachloride. Evaporation of the filtrate and washings gave an oil (7.4 g). Without further purification the oil was dissolved in ether (45 cm^3) and the solution cooled to 0 °C. Triethylamine (4.5 g, 45 mmol) in ether (4.5 cm^3) was added dropwise to the latter and the resulting suspension stirred for 2 h. The solids were filtered off, the filtrate washed with water, dried ($MgSO_4$) and evaporated to give an oil (2.9 g). Chromatography of the latter on silica with benzene–hexane (1:1) gave the title compound as an oil (632 mg, 12%); δ_H(90 MHz) 7.50–7.0 (4 H, m, ArH), 5.65 (1 H, q, *J* 2) and 2.20 (3 H, d, *J* 2). Further elution gave 3-methyleneindan-1-one (417 mg, 8%); δ_H(90 MHz) 7.9–7.25 (4 H, m, ArH), 5.8 (1 H, m), 5.3 (1 H, m) and 3.25 (3 H, m).

3-*Methyl*-3-(1-*naphthyl*)*indan*-1-*one* **12**.—Butyllithium (1.6 mol dm^{-3} solution in hexane; 3.6 cm^3, 5.8 mmol) was added to a solution of 1-bromonaphthalene (1.435 g, 6.9 mmol) in ether (9.5 cm^3), and the mixture stirred for 30 min. The suspension with the aid of ether (13 cm^3) was added to a suspension of copper(I) bromide–dimethyl sulfide complex (596 mg, 2.9 mmol) in ether (9.5 cm^3) at −20 °C. After 20 min dimethyl sulfide (18.5 cm^3) was syringed into the mixture and the resulting solution cooled to −55 °C. A solution of 3-methylindenone (417 mg, 2.9 mmol) in ether (9.5 cm^3) was then added to the mixture which after 85 min was warmed to −7 °C and stirred for 45 min before being allowed to warm to room temperature. The solution was poured into saturated aqueous ammonium chloride and extracted into ether. The ether extract was washed with 2 mol dm^{-3} aqueous sodium hydroxide and water, dried ($MgSO_4$) and evaporated to give an oil (1.34 g). Chromatography of the latter on silica with benzene–hexane (6:4) gave the title compound as an oil (286 mg, 36%); m.p. 137 °C (from ether) (Found: C, 87.95; H, 5.9; M^+, 272.119. $C_{20}H_{16}O$ requires: C, 88.2; H, 5.9%; *M*, 272.120); ν_{max}(Nujol)/cm^{-1} 1720, 1590, 1270, 1230 and 760; δ_H(90 MHz) 8.00–7.05 (11 H, m, ArH), 3.5 (1 H, d, *J* 18), 2.95 (1 H, d, *J* 18) and 1.93 (3 H, s); *m/z* 272, 257, 228, 145, 128, 115, 101, 91, 77 and 69 (67.5, 100.0, 26.7, 18.2, 24.4, 44.6, 26.8, 28.3, 36.3 and 13.4%).

1,3-*Dimethyl*-1-(1-*naphthyl*)*indene*.—Iodomethane (477 mg, 3.7 mmol) in ether (3 cm^3) was added to magnesium turnings (50.4 mg, 2.1 mmol), and the mixture refluxed until no magnesium remained. After the mixture had been cooled to 0 °C, the foregoing ketone (286 mg, 1.1 mmol) in ether (8 cm^3) was added to it and the whole refluxed for 100 min; a further equivalent of methylmagnesium iodide solution was then added to it. A further equivalent of methylmagnesium iodide was added after 40 min of refluxing and the solution refluxed for 10 min. The mixture was poured onto 2 mol dm^{-3} sulfuric acid and ice and then extracted into ether. The ether extracts were washed with 1 mol dm^{-3} aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$) and evaporated to give an oil (310 mg). The oil was dissolved in benzene (30 cm^3) and tosic acid (50 mg) added. This solution was refluxed for 15 min and then poured into 1 mol dm^{-3} aqueous sodium carbonate and extracted with ether. The extract was washed with water, dried ($MgSO_4$) and evaporated to give an oil (358 mg). Chromatography of the latter on silica with hexane gave the title compound (229 mg, 77%) which solidified with time; m.p. 97–98 °C (from ether–methanol) (Found: C, 93.3; H, 6.6; M^+, 270.140. $C_{21}H_{18}$ requires C, 93.3; H, 6.7%; *M*, 270.141); ν_{max}(Nujol)/cm^{-1} 3040, 1595, 1500, 800, 740 and 700; δ_H(90 MHz) 7.85–6.90 (11 H, m, ArH), 6.38 (1 H, q, *J* 2), 2.20 (3 H, d, *J* 2) and 1.75 (3 H, s); *m/z* 270, 255, 239, 226, 142, 126, 120, 113, 101 and 77 (100.0, 73.1, 36.3, 7.1, 22.6, 28.7, 23.7, 10.8, 7.2 and 12.6%).

1,3-*Dimethyl*-2-(1-*naphthyl*)*indene*.—A solution of 1,3-dimethyl-1-(1-naphthyl)indene (18 mg, 0.06 mmol) in deuteriobenzene (*ca.* 0.4 cm^3) was degassed in a small bore tube and the tube sealed under vacuum. After being heated for 10 h 20 min at 316 °C the tube was opened, the solvent evaporated and the residue chromatographed on silica with hexane to give the title compound as an oil (13 mg, 72%) (Found: M^+, 270.140. $C_{12}H_{18}$ requires *M*, 270.140); ν_{max}(film)/cm^{-1} 1600, 1500, 800, 780, 760, 740 and 700 cm^{-1}; δ_H(90 MHz) 8.00–7.10 (11 H, m, ArH), 3.90 (1 H, q q, *J* 7 and 2), 1.90 (3 H, d, *J* 2) and 1.15 (3 H, d, *J* 7); *m/z* 270, 255, 239, 141, 129, 120, 115 and 91 (100.0, 60.4, 32.2, 12.8, 14.0, 18.1, 8.5 and 7.8%).

Preparation of the Alcohol from **14** *and* **1** (X = CHO).—2-(2-Bromoethyl)-1,3-dioxolane (956 mg, 5.3 mmol) in tetrahydrofuran (6 cm^3) was added to magnesium turnings (121 mg, 5 mmol) and the mixture heated at 30–35 °C for 1 h. The Grignard reagent was then added to a solution of (+)-1,3-dimethylindene-1-carbaldehyde (500 mg, 2.9 mmol) in ether (5 cm^3) at −78 °C. After 80 min the solution was warmed to room temperature, diluted with ether and poured into brine. The aqueous phase was extracted with ether, and the combined extracts were washed with water, dried ($MgSO_4$), and evaporated to give an oil (724 mg). Chromatography of the latter on silica with ether–hexane (1:1) gave the alcohol as an oil (329 mg, 41%); m.p. 81–82 °C (from ether–hexane); $[\alpha]_D^{24}$ +72 (*c* 2.44 in C_6H_6) (Found: C, 74.5; H, 8.3%; M^+, 274.156. $C_{17}H_{22}O_3$ requires C, 74.5; H, 8.0%; *M*, 274.157); ν_{max}(film)/cm^{-1} 3480 and 760; δ_H(90 MHz in C_6D_6) 7.30 (4 H, m, ArH), 6.22 (1 H, q, *J* 2), 4.68 (1 H, t, *J* 4), 3.80 (1 H, m), 3.44 (4 H, m), 2.65 (1 H, s), 2.02 (3 H, d, *J* 2), 1.64 (4 H, m) and 1.59 (3 H, s); *m/z* 274, 169, 156, 144, 131, 115, 87, 73 and 69 (0.2, 9.6, 5.9, 100.0, 84.5, 10.1, 48.5, 28.6 and 61.1%).

Preparation of the Ketone **15** [X = $O(CH_2)_2O$].—A solution of pyridine (1.33 g, 16.8 mmol) in dichloromethane (89 cm^3) was cooled to 0 °C and chromium trioxide (0.8 g, 8.4 mmol) added to it, the mixture was then stirred at room temperature for 20 min. The foregoing alcohol (329 mg, 1.2 mmol) was dissolved in dichloromethane (12 cm^3) and added to the mixture. After being stirred for 40 min the solution was diluted with ether and washed consecutively with 1 mol dm^{-3} aqueous sodium carbonate, 1 mol dm^{-3} hydrochloric acid, 1 mol dm^{-3} aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$) and evaporated to give an oil (315 mg). Chromatography of the latter on silica with hexane–ether (7:3) gave the ketone **15** [X = $O(CH_2)_2O$] as an oil (262 mg, 80%); $[\alpha]_D^{24}$ +123 (*c* 2.09 in C_6H_6) (Found: M^+, 272.141. $C_{17}H_{20}O_3$ requires *M*, 272.141); ν_{max}(film)/cm^{-1} 1700, 1140 and 760; δ_H(90 MHz in C_6D_6) 7.30 (4 H, m, ArH), 5.91 (1 H, q, *J* 2), 4.80 (1 H, t, *J* 4), 3.44 (4 H, m), 2.20 (4 H, m), 2.03 (3 H, d, *J* 2) and 1.71 (3 H, s); *m/z* 272, 143, 129, 85 and 73 (1.9, 9.0, 100.0, 38.1 and 9.3%).

Preparation of the 1,4-*Dicarbonyl Compound* **15** (X = O).—A solution of potassium periodate (1.6 g) in 3 mol dm^{-3} sulfuric acid (2 cm^3) in water (100 cm^3) was prepared and a portion (11 cm^3) was mixed with a solution of the foregoing keto acetal (101 mg, 0.36 mmol) in dioxane (26 cm^3); the mixture was then heated for 6 h at 70–75 °C. The solution was cooled, diluted with ether and poured into 1 mol dm^{-3} aqueous sodium hydrogen carbonate. The aqueous phase was extracted with ether and the combined extracts were washed with water, dried ($MgSO_4$) and evaporated to give an oil (90 mg). Flash chromatography of the latter on silica with hexane–ether (6:4) gave **15** (X = O) as an oil (58 mg, 69%); $[\alpha]_D^{24}$ +107 (*c* 2.92 in C_6H_6) (Found: M^+, 228.115. $C_{15}H_{16}O_2$ requires *M*, 228.115); ν_{max}(film)/cm^{-1} 2960, 1710, 1020 and 760; δ_H(90 MHz in C_6D_6) 9.39 (1 H, s), 7.30 (4 H, m), 5.99 (1 H, q, *J* 2), 2.20 (4 H, m), 2.04 (3 H, d, *J* 2) and 1.64 (3 H, s); *m/z* 228, 143, 141, 128, 115 and 85 (9.5, 51.7, 10.8, 35.8, 11.6 and 100%).

(+)-1,3-*Dimethyl*-1-(N-*propylpyrrol*-2-*yl*)*indene* **13**.—To a solution of dicarbonyl compound **15** (X = O) (28.8 mg, 0.13 mmol) in methanol (1 cm^3) was added propylamine (11.5 mg, 0.19 mmol) and glacial acetic acid (2 drops). After 100 min the mixture was diluted with ether and poured into 1 mol dm^{-3} aqueous sodium hydrogen carbonate. The aqueous layer was extracted with ether and the combined extracts were washed with water, dried ($MgSO_4$) and evaporated to give an oil (54 mg). Flash chromatography of this on silica with hexane–ether (99:1) gave the title compound as an oil (13 mg, 40%); $[\alpha]_D^{24}$ +213 (*c* 0.66 in C_6H_6) (Found: M^+, 251.168. $C_{18}H_{21}N$ requires *M*, 251.167); ν_{max}(film)/cm^{-1} 2970, 1470, 1305, 760 and 715; δ_H(90 MHz in C_6D_6) 7.30 (4 H, m, ArH), 6.60 (3 H, m), 6.10 (1 H, q, *J* 2), 3.40 (2 H, t, *J* 6), 2.02 (3 H, d, *J* 2), 1.80 (3 H, s), 1.20 (2 H, m, *J* 6) and 0.50 (3 H, t, *J* 6); *m/z* 251, 236, 222, 208, 194, 178, 165, 152, 142, 128, 115 and 80 (100.0, 78.0, 11.1, 17.5, 28.0, 11.9, 23.1, 12.0, 22.3, 16.3, 10.1 and 16.1%).

Thermolysis of (+)-1,3-*Dimethyl*-1-(N-*propylpyrrol*-2-*yl*)*indene* **13**.—A solution of (+)-1,3-dimethyl-1-(*N*-propylpyrrol-2-yl)indene (13 mg, 0.05 mmol) in deuteriobenzene (*ca.* 0.4 cm^3) was degassed in a small bore tube, and the tube sealed under vacuum. The tube was heated for 62 min at 320 °C. Small changes in the material were observed by NMR. Chromatography on silica with hexane–ether (99:5) gave (+)-1,3-dimethyl-1-(*N*-propylpyrrol-2-yl)indene as an oil (8.6 mg, 66%); $[\alpha]_D^{24}$ +208 (*c* 0.43 in $CHCl_3$).

Preparation of 3-(2-*Furyl*)-3-*methylindan*-1-*one*.—Butyllithium (1.6 mol dm^{-3} solution in hexane; 3.48 cm^3, 5.6 mmol) was added to a solution of furan (756 mg, 11 mmol) in ether (10 cm^3) at −20 °C, and the yellow suspension stirred at room temperature for 4 h. The mixture was added to a suspension of copper(I) bromide–dimethyl sulfide complex (572 mg, 2.8 mmol) in ether (10 cm^3) at −30 °C, and the solution stirred for 1 h. Dimethyl sulfide (17.6 cm^3) was then added and the solution cooled to −60 °C. A solution of 3-methylindenone (200 mg, 1.4 mmol) in ether (5 cm^3) was syringed into the mixture, and the solution stirred for 85 min. The mixture was warmed to 0 °C for 20 min and then to room temperature. The mixture was diluted with ether and poured into saturated aqueous ammonium chloride. The aqueous layer was extracted with ether and the combined extracts were washed consecutively with 2 mol dm^{-3} aqueous sodium hydroxide and water, dried ($MgSO_4$) and evaporated to give an oil (275 mg). Chromatography of the latter on silica with hexane–ether (95:5) gave the title compound as an oil (109 mg, 37%) (Found: M^+, 212.083. $C_{14}H_{12}O_3$ requires *M*, 212.084); ν_{max}(film)/cm^{-1} 1710, 1600, 1290, 1240 and 740; δ_H(90 MHz) 7.50 (5 H, m, ArH), 6.35 (1 H, d, *J* 2), 6.15 (1 H, d, *J* 2), 3.30 (1 H, d, *J* 18), 2.80 (1 H, d, *J* 18) and 1.80 (3 H, s); *m/z* 212, 197, 169, 141, 128, 115 and 94 (43.8, 100.0, 11.1, 28.1, 60, 33.8 and 21.5%).

1-(2-*Furyl*)-1,3-*dimethylindene* **1** (X = 2-furyl).—The foregoing ketone was treated with methylmagnesium iodide and the resulting alcohol dehydrated as described above for the preparation of 1,3-dimethyl-1-(1-naphthyl)indene. Chromatography of the product on silica with hexane gave the title compound as an oil (55 mg, 52%) (Found: M^+, 210.104. $C_{15}H_{14}O$ requires: *M*, 210.104); ν_{max}(film)/cm^{-1} 1500, 1150, 1010, 760 and 740; δ_H(90 MHz) 7.30 (5 H, m, ArH), 6.20 (2 H, m), 6.00 (1 H, m), 2.20 (3 H, d, *J* 2) and 1.63 (3 H, s); *m/z* 210, 195, 165, 152, 141, 128, 115 and 83 (86.0, 100.0, 42.3, 23.1, 8.1, 10.6, 10.5 and 7.4%).

3-*Methyl*-3-(2-*thienyl*)*indan*-1-*one*.—This compound was

prepared starting from thiophene and 3-methylindan-2-one in the manner described above for the preparation of 3-(2-furyl)-3-methylindan-1-one from furan and the same ketone. Chromatography on silica with hexane–ether (95:5) gave the title compound as an oil (85 mg, 27%) (Found: M^+, 228.060. $C_{14}H_{12}OS$ requires M, 228.061); ν_{max}(film)/cm^{-1} 2980, 1710, 1600, 1460, 1300, 1240 and 710; δ_H(90 MHz) 8.00–6.85 (7 H, m, ArH), 3.30 (1 H, d, J 16), 3.00 (1 H, d, J 16) and 2.05 (3 H, s); m/z 228, 213, 184, 152, 145, 115, 92, 77 and 63 (42.2, 100.0, 20.8, 9.6, 18.2, 23.4, 8.4, 7.9 and 6.0%).

Preparation of 1,3-*Dimethyl*-1-(2-*thienyl*)*indene* **1** (X = 2-thienyl).—The foregoing ketone was treated with methylmagnesium iodide and the resulting alcohol dehydrated as described above for the preparation of 1,3-dimethyl-1-(1-naphthyl)indene. The title compound **1** (X = 2-thienyl) was obtained as an oil (51%) (Found: M^+, 226.081. $C_{15}H_{14}S$ requires M, 226.082); ν_{max}(film)/cm^{-1} 1470, 1240, 760 and 700; δ_H(90 MHz) 7.40–6.75 (7 H, m, ArH), 6.15 (1 H, q, J 2), 2.10 (3 H, d, J 2) and 1.70 (3 H, s); m/z 226, 211, 178, 165, 152, 141, 128, 115, 89, 77 and 69 (73.9, 100.0, 34.7, 24.4, 14.3, 10.3, 13.6, 14.8, 7.3, 9.7 and 8.3%).

Thermolysis of **1** (X = 2-thienyl) *and* **1** (X = 2-furyl).—The rearrangement of **1** (X = 2-thienyl) was followed using the NMR method described in the general directions. The integrals for the vinylic methyl in the starting material (δ 2.08) and product (δ 2.38) were carefully monitored. The other signals expected for **3** (X = 2-thienyl) were observed at 1.40 (3 H, d, J 7) and 3.74 (1 H, q q, J 7 and 2). Similar characteristic peaks were observed in the thermolysis of **1** (X = 2-furyl) and the integrals of the signals at δ 1.95 for the starting material and δ 2.35 for the product used to determine the rate constant of the reaction. Both rearrangements were conducted in C_6D_6 at 320 °C.

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