# o-Quinonoid Compounds. Part 16.[1] 1,5-Shift of Vinyl Groups in 1,3-Dimethylindenes; Product Studies and Migratory Aptitudes of Substituted Vinyl Groups

By Douglas J. Field and David W. Jones,* Department of Organic Chemistry, The University, Leeds LS2 9JT

Several 1-vinylindenes (1; X = substituent) undergo clean thermal rearrangement to 2-vinylindenes (2; X = Me, Ph, $C_6H_4NO_2$-p, CHO, CO_2Et, CN, CO_2Ph, COPh, CONHMe, and COMe). Racemisation rates for the optically active indenes E-(1) provide migratory aptitudes for E-substituted-vinyl groups in the 1,5-shift leading to the 2H-indene intermediates (2). The migratory aptitude of $CH=CH_2$ is much greater than that of Ph, and E-substituents on a vinyl group produce much larger effects than p-substituents on a phenyl ring. Migratory aptitudes of E-(CH=CHX) correlate with σ_R^- values of the substituent X, as well as with the rates of morpholine addition to the olefins $CH_2=CHX$ and the pK_a of the carbon acids CH_3X. The activating effect of X on the 1,5-vinyl shift is similar to its effect on the dienophilic character of olefins (COCl > COPh > COMe > CN > CO_2R > H > Me). Z-Vinyl groups migrate faster than the corresponding E-vinyl groups in accord with preferred migration via an exo-arrangement (4).

MARKED differences in the migratory aptitudes of unsaturated groups towards 1,5-sigmatropic shift (HCO $\gg$ MeCO $\gg$ CH=CH$_2$ or CO$_2$Me) [2,3] can be explained in part by assuming transition state (TS) interaction between the π*-orbital of the migrating group and the HOMO of the diene system.[2] However, for the migrating groups studied so far, resonance, inductive, steric, bond-strength, and secondary interaction effects [2] may differ. To investigate variations of migratory aptitude with the electron-accepting ability of the migrating group, while keeping other effects fairly constant, we sought to study racemisation of the E-vinyl-substituted indenes (1) [4] (Scheme). Although no examples of 1,5-vinyl shift were

(1)   (2)

(3)

SCHEME
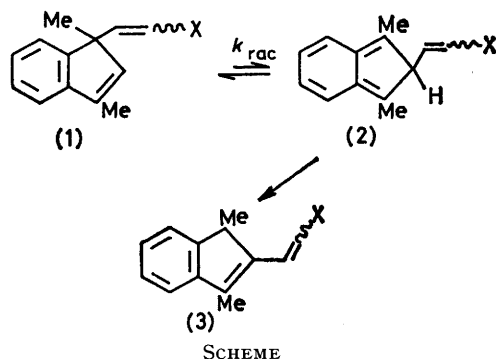
known at the outset of our work, examples of 1,5-acyl [2] and 1,5-aryl [5] shifts encouraged our attempts to observe vinyl migration. In the meantime an example of 1,5-vinyl migration has appeared,[6] and 1,5-butadienyl shifts have been recognised.[7] More recently an example of 1,5-vinyl migration in a simple cyclopentadiene has been investigated mechanistically.[8] We expected that the E-vinyl substituted indenes (1) would racemise by 1,5-shift of the vinyl group to give the transient and symmetric isoindenes (2), which by 1,5-hydrogen shift would give the 2-vinylindenes (3) (Scheme). By employing racemisation rates rather than rates of formation of the 2-vinylindenes we would ensure reliable

migratory aptitude data even in those cases in which hydrogen shift was slower than vinyl migration in the 2H-indene intermediates (2).[9]

RESULTS AND DISCUSSION

Preparation and Thermolysis of the 1-*Vinylindenes.*—The required 1-vinylindenes were generally prepared from optically active 1-formyl-1,3-dimethylindene [2] by Wittig or Wadsworth–Emmons reactions. 1-Isopropenyl-1,3-dimethylindene was similarly prepared from (+)-1-acetyl-1,3-dimethylindene.[2] Sodium triethyl phosphonoacetate reacted with 1-formyl-1,3-dimethylindene to give E-(1; X = CO$_2$Et) in excellent yield (85%) and this was converted into E-(1; X = CHO) by reduction with lithium aluminium monoethoxy-hydride [10] followed by oxidation (CrO$_3$–pyridine–CH$_2$Cl$_2$). Reaction of E-(1; X = CHO) with methyl and phenyl Grignard reagents and oxidation of the resulting alcohols (CrO$_3$–2 pyridine–CH$_2$Cl$_2$) gave E-(1; X = COMe) and E-(1; X = COPh). Saponification of E-(1; X = CO$_2$Et) gave the corresponding acid which was converted into E-(1; X = COCl) and hence the amide (1; X = CONHMe) by reaction with methylamine, and the ester (1; X = CO$_2$Ph) by reaction with sodium phenoxide. The preparation of (+)-1,3-dimethyl-1-vinylindene, Z- and E-(+)-1-chlorovinyl-1,3-dimethylindene, and Z- and E-(+)-1-methoxyvinyl-1,3-dimethylindene were described earlier.[2] Mixtures of Z- and E-olefins were separated by short-column chromatography [11] on Kieselgel G (Merck) or Kieselgel G–silver nitrate (see Experimental section).

On thermolysis the majority of the E-1-vinylindenes listed in the Table underwent clean loss of optical activity and when thermolysis was prolonged the corresponding E-2-vinylindenes could be isolated in good yield. Racemisations generally followed first-order kinetics providing good straight-line plots. Although racemisations of (1; X = H) provided good first-order plots, the 2-vinylindene (3; X = H) was not isolated after prolonged heating at 210 °C. The n.m.r. spectrum

of the product indicated a mixture, and the mass spectrum the presence of dimeric material; 1-phenyl-butadiene is known [12] to dimerise readily even at 80 °C. Racemisation of E-(1; X = Cl) could not be accurately followed, since on prolonged heating a strong colour developed which the polarimeter could not penetrate. The quoted rate constant [Table entry (xviii)] is the average of three one-point rate constants each obtained after 18 h heating at 180 °C (ca. 7.5% racemisation). Attempts to obtain rate constants for racemisation of E-(1; X = OMe) failed due to its rapid interconversion with the Z-isomer at the temperatures required (>220 °C). On heating, all the Z-1-vinylindenes gave mixtures of Z- and E-2-vinylindenes, the quantity of E-product increasing with continued heating. To test if all the 2-E-isomer was formed via the 2-Z-isomer the thermolysis of Z-(1; X = Ph) was studied in detail. A sample of Z-(1; X = Ph) was heated at 180 °C and the amounts of starting material, Z-(3; X = Ph), and E-(3; X = Ph) present after three time intervals determined by n.m.r. measurements. The rate constant for disappearance of Z-(1; X = Ph) was found to be 5.41×10^{-5} s^{-1} (k_1). The isomer Z-(3; X = Ph) was isolated from the resulting mixture by chromatography and the rate constant for Z–E isomerisation to E-(3; X = Ph) determined as 1.49×10^{-5} s^{-1} (k_2). For two consecutive first-order reactions as in equation (E1) the amount of C present at time t is given [13] by equation (E2). On the

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \qquad (E1)$$
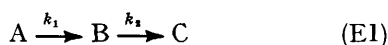
$$[C] = \frac{[A]_0}{k_2 - k_1} \times$$
$$\left\{ k_2[1 - \exp(-k_1 t)] - k_1[1 - \exp(-k_2 t)] \right\} \quad (E2)$$

basis of equation (E2) the amounts of E-(3; X = Ph) that should be present after heating Z-(1; X = Ph) for 5.27, 9.08, and 14 h are respectively 9.6, 21.8, and 37.5%. The amounts of E-(3; X = Ph) actually observed after these time intervals are respectively 11, 22, and 33%. The rate of conversion of Z-(3; X = Ph) into the E-isomer thus quantitatively accounts for the E-(3; X = Ph) present during the thermolysis of Z-(1; X = Ph). The conversion of Z-(1; X = Ph) into (3; X = Ph) is therefore highly stereoselective, in accord with the occurrence of concerted 1,5-vinyl migration. The intervention of configurationally unstable vinyl radicals [14] in the rearrangement is therefore unlikely.

Discussion of Migratory Aptitude Data.—Rate data and derived activation parameters for racemisation of the vinylindenes (1) are detailed in the Table. The activation enthalpies fall in the range 28.6—33.9 kcal mol^{-1} and the activation entropies are uniformly negative and vary between −13.2 and −10.26 cal K^{-1} mol^{-1}. The activation parameters therefore favour racemisation by concerted 1,5-vinyl shift to an isoindene (2) rather than by dissociation to radicals or ions which recombine at C-1, C-2, and C-3 of the indene system. The data show that electron-withdrawing groups increase the

rate of vinyl migration; E-(1; X = CHO) racemises 132 times more rapidly than (1; X = H) at 180 °C, and a p-nitro-group accelerates E-β-styryl migration by ca. 3.4 [Table, entries (iii) and (iv)]. On the other hand electron-donating groups slow down migration. An E-methyl group [entry (ii)] slows the vinyl shift by a factor of 0.58, and although accurate rate data were not obtain-

Rate data for racemisation of the vinylindenes (1) (in diphenyl ether solvent unless otherwise stated)

Vinylindene (1) X	$10^5 k_{rac.}/\text{s}^{-1}$ at stated temperature (°C)	$\Delta S^{\ddagger}/\text{cal}$ K^{-1} mol^{-1}	$\Delta H^{\ddagger}/$ kcal mol^{-1}
(i) H	1.79 (210)	−11.09	33.85
	3.37 (220)	±3.28	±1.64
	7.89 (230)		
	14.29 (240)		
	0.003 75 (140) [a]		
	0.1575 (180) [a]		
(ii) E-Me	4.62 (230)		
(iii) E-Ph	5.69 (200)	−12.90	31.15
	12.06 (210)	±1.02	±0.49
	23.34 (220)		
	44.03 (230)		
	1.277 (180) [a]		
(iv) E-$C_6H_4NO_2$-p	40.78 (210)		
(v) E-CHO	4.58 (160)	−12.56	28.79
	9.94 (170)	±0.33	±0.15
	20.73 (180)		
	43.08 (190)		
	0.859 (140) [a]		
(vi) E-CHO (in dimethyl sulphoxide)	23.69 (170)		
(vii) E-CO$_2$Et	4.37 (180)	−10.75	31.02
	9.33 (190)	±0.38	±0.18
	19.79 (200)		
	39.44 (210)		
	0.141 (140) [a]		
(viii) E-CN	5.21 (180)		
(ix) E-CO$_2$Ph	10.99 (180)		
(x) E-COPh	34.94 (180)		
(xi) E-CONHMe	4.36 (190)		
	2.05 (180) [b]		
(xii) E-COMe	27.49 (190)		
	13.30 (180) [b]		
(xiii) E-COCl (in xylene)	ca. 1.92 (140)		
(xiv) Z-Me	21.93 (230)		
(xv) Z-Ph	6.28 (180)	−10.26	30.91
	13.95 (190)	±0.75	±0.35
	28.49 (200)		
	56.90 (210)		
(xvi) Z-$C_6H_4NO_2$-p	3.67 (160)	−13.22	28.69
	8.09 (170)	±0.53	±0.24
	17.12 (180)		
	34.04 (190)		
(xvii) Z-Cl	1.31 (180)		
(xviii) E-Cl	ca. 0.127 (180)		
(xix) 1-isopropenyl-1,3-dimethyl-indene	2.24 (240)		

[a] Value extrapolated using the given activation parameters.
[b] Value estimated using the activation parameters of entry (v).

able (see above), an E-methoxy- and an E-chloro-substituent [entry (xviii)] both appear to retard vinyl migration. These latter observations indicate that the *resonance* electron-withdrawing ability of X is more important than its inductive effect in determining migratory aptitude. Indeed no correlation was found

between the σ_I value [15] of the group X and the migratory aptitude of E-(CH=CHX) whereas a good correlation (correlation coefficient $r = 0.966$) between σ_R^- values of X [16] and the migratory aptitudes of seven E-vinyl groups (X = H, Cl, CO_2Et, CN, CONHMe, $COCH_3$, and CHO) was observed. Less satisfactory correlation ($r = 0.896$) was obtained using σ^- values (X = H, Cl, Ph, CONHMe, CO_2Et, $COCH_3$, CN, CHO) [15] which include a contribution from the inductive effect of X. The ρ-value
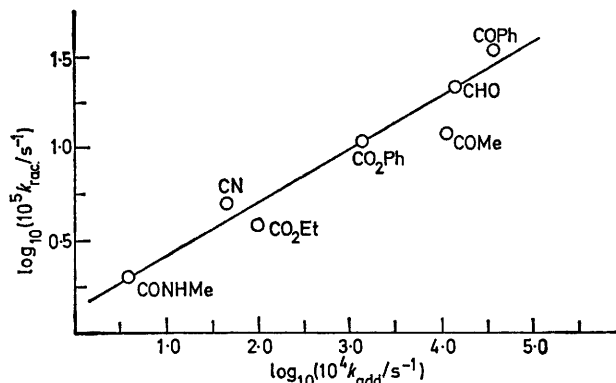

FIGURE 1 Plot of $\log_{10}10^5k_{rac.}$ for racemisation of the indenes (1) at 180 °C vs. $\log_{10}10^4k_{add.}$ for addition of morpholine to the olefins CH_2=CHX (ref. 17)

obtained in this correlation ($+ 1.90$) indicates little charge development in the rearrangement TS. Better correlations were obtained between racemisation rates and the rates of morpholine addition to the olefins CH_2=CHX (Figure 1, $r = 0.976$), and the pK_a of the CH_3X carbon acids [17] (Figure 2, $r = 0.970$). Correlation of migratory aptitude with the resonance electron-accepting ability of the group X supports the view [8,18]
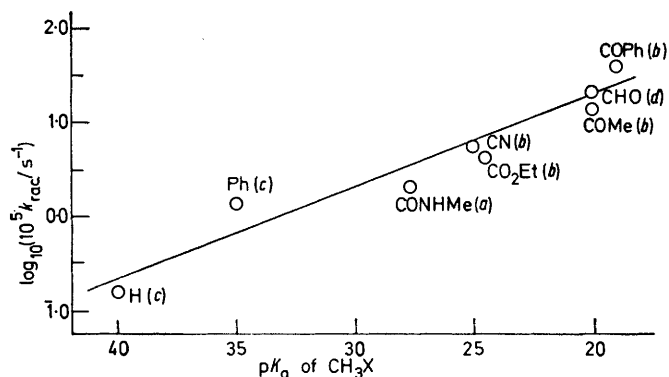

FIGURE 2 Plot of $\log_{10}10^5k_{rac.}$ for racemisation of the indenes (1) at 180 °C vs. the pK_a values of the carbon acids CH_3X. pK_a values, after (a) ref. 17; (b) R. G. Pearson and R. L. Dillon, J. Amer. Chem. Soc., 1953, 75, 2439; (c) D. J. Cram, 'Fundamentals of Carbanion Chemistry,' Academic Press, New York, 1965; and (d) K. F. Bonhoeffer, K. H. Geib, and O. Reitz, J. Phys. Chem., 1939, 7, 664

that more rapid rearrangement of unsaturated than saturated groups is, at least in part, associated with secondary interaction (2y) involving the π^* orbital of the migrating group [see (4)]. However, this interaction

does not appear to be associated with appreciable separation of charge; E-(1; X = CHO) racemises only 2.38 times faster in dimethyl sulphoxide than in diphenyl ether [Table, entries (v) and (vi)], and whilst morpholine addition to CH_2=CHX is accelerated by ca. 10^4 in going from X = CONHMe to X = COPh, the same substituent change produces an increase of only $10^{1.25}$ in the racemisation rate of E-(1) (Figure 1). Changes of substituent and solvent likewise produce only small changes in the rates of Diels–Alder reactions where interaction of only one pair of frontier MO's is also believed to be


(4)
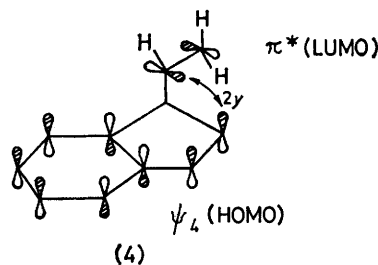
important.[19] Thus the addition of styrene to hexachlorocyclopentadiene is only twice as fast in dimethylformamide as in toluene,[20] and for E-disubstituted ethylenes (XCH=CHX) dienophilicity towards cyclopentadiene (at 20 °C) increases by a rate factor of 18 in going from X = CO_2Me ($k_{rel.}$ 1.00), through X = CN ($k_{rel.}$ 1.1) and COMe ($k_{rel.}$ 4.0), to X = COPh.[20] The activating effect of substituents on 1,5-vinyl shift is therefore similar to the effect of the same substituents on the dienophilic character of olefins. In both the Diels–Alder reaction and the 1,5-vinyl shift the activating effect of the substituents increases in the order: H ≪ CO_2R < CN < COMe < COPh < COCl.

It appears that vinyl migration (1; X = H) occurs ca. 900 times faster than phenyl migration in 1-methyl-1-phenylindene ($k = 8.0 \times 10^{-5}$ s⁻¹, 300 °C, Ph_2O),[5] and that the substituent effects observed here (Table) for

(5)
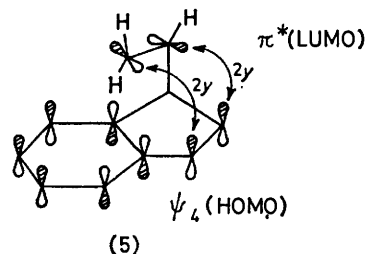
E-substituted vinyl groups are much larger than those observed earlier [21] for migration of p-substituted aryl groups in substituted indenes. Comparisons of racemisation rates for corresponding E- and Z-olefins favours the suggestion that rearrangement preferentially involves an exo-arrangement of the migrating π-system and the indene fragment as in (4) rather than an endo-arrangement (5) which would be destabilised by repulsive

secondary (HOMO–LUMO) interactions.* The Table [entries (ii) and (xiv), (iii) and (xv), and (iv) and (xvi)] shows that Z-olefins racemise 4.2—4.9 times faster than their E-counterparts. Table entries (xvii) and (xviii) suggest that k_Z/k_E increases to $ca.$ 10 for X = Cl, but $k_{rac.}$ for E-(1; X = Cl) is subject to uncertainty (see above). For a Z-olefin steric destabilisation would be expected to increase markedly in going to an $endo$-TS. For an E-olefin the increase in steric destabilisation in going to an $endo$-TS should be less, and the E-olefins should then rearrange the more rapidly, contrary to our observations. On the other hand in going to an exo-TS a Z-olefin would be expected to experience the greater decrease in steric interaction and so rearrange more rapidly than its E-isomer, as is observed. Comparison of entries (iii) and (iv) and (xv) and (xvi) shows that a p-nitro-group is only slightly less effective at promoting migration of the Z-styryl group (rate increase 2.7) than

(6)   (7)
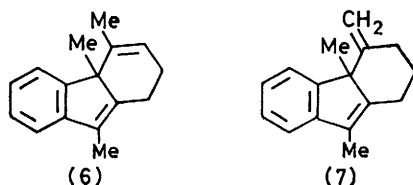
the E-styryl group (rate increase 3.4). This suggests comparable conjugation of the nitro and aryl groups and the double bond at the TS for migration of Z- and E-styryl groups. Whilst this is possible for an exo-TS, steric factors would be expected severely to curtail such conjugation in the $endo$-TS of Z-styryl migration. We have obtained further evidence on this point by synthesis of the olefins (6) and (7) in optically active form; at 250 °C (6), constrained to migrate via an exo-TS, racemised $ca.$ 50 times faster than (7) which must rearrange via an $endo$-TS.[23]

EXPERIMENTAL

M.p.s were determined with a Kofler hot stage apparatus. Unless otherwise specified, i.r. spectra refer to films, and n.m.r. spectra to solutions in deuteriochloroform measured with a Perkin-Elmer R 12 (60 MHz) or R 32 (90 MHz) spectrometer. Mass spectra were obtained with an A.E.I. MS 902 instrument. Where accurate mass measurement was used to establish molecular formulae the purity of the sample was checked by t.l.c. in more than one solvent system, as well as by n.m.r. and i.r. spectroscopy. Petroleum refers to light petroleum (b.p. 60—80 °C) and chromatography on silica to short-column chromatography[11] over Kieselgel G (Merck). Optical rotations were obtained using a Perkin-Elmer 141 or Thorn type 243 polarimeter. Kinetic measurements were made as previously described.[2]

Thermolyses (xi), (xii), and (xiii) were conducted on solutions first used for kinetic measurements which result in loss of up to 50% of material. The yields of 2-vinyl-indenes obtained in these experiments therefore represent minimum values.

$(+)$-1,3-$Dimethyl$-1-Z-$propenylindene$ and $(+)$-1,3-$Dimethyl$-1-E-$propenylindene$.—Butyl-lithium (205 mg, 3.2 mmol) in hexane (1.5 ml) was syringed into a stirred slurry of ethyltriphenylphosphonium bromide (1.3 g, 3.5 mmol) in ether (50 ml) at 0 °C under nitrogen. After stirring at 0 °C (2 h), $(+)$-1-formyl-1,3-dimethylindene[2] (420 mg, 2.44 mmol) in ether (6 ml) was added and stirring continued (45 min). The product was washed with water, and the ether layer dried (MgSO$_4$) and evaporated. Chromatography of the product (1.08 g) on 20% silver nitrate–silica (60 g) in benzene–petroleum (1 : 9) gave first $(+)$-1,3-$dimethyl$-1-E-$propenylindene$ (125 mg) as a colourless oil (Found: M^+, 184.125 0. $C_{14}H_{16}$ requires M, 184.125 2); $\nu_{max.}$ 1 619 and 968 cm^{-1}; τ(60 MHz) 2.75 (4 H, s, aromatic), 3.99 (1 H, q, J 1.5 Hz), 4.48 (2 H, m, olefinic), 7.91 (3 H, d, J 1.5 Hz), 8.38 (3 H, m), and 8.66 (3 H, s); $[\alpha]_D^{24}$ $+18.0°$ (c 1.03, CHCl$_3$).

Continued elution of the column gave $(+)$-1,3-$dimethyl$-1-Z-$propenylindene$ (155 mg) as an oil (Found: M^+, 184.125 0); $\nu_{max.}$ 1 617 and 1 647 cm^{-1}; τ(60 MHz) 2.78 (4 H, m, aromatic), 3.87 (1 H, q, J 1.5 Hz), 4.39 (1 H, dq, J 11 and 1 Hz), 4.63 (1 H, dq, J 11 and 6.5 Hz), 7.91 (3 H, d, J 1.5 Hz), 8.61 (3 H, s), and 8.84 (3 H, dd, J 6.5 and 1 Hz); $[\alpha]_D^{24}$ $+209°$ (c 1.436, CHCl$_3$).

$(+)$-1,3-$Dimethyl$-1-Z-$styrylindene$ and $(+)$-1,3-$Dimethyl$-1-E-$styrylindene$.—Butyl-lithium (160 mg, 2.5 mmol) in hexane (1.0 ml) was added to a stirred slurry of benzyl-triphenylphosphonium chloride (1.125 g, 2.9 mmol) in dry ether (125 ml) at 20 °C under nitrogen. After stirring (2 h) at 20 °C, $(+)$-1-formyl-1,3-dimethylindene[2] (250 mg, 1.45 mmol) in ether (5 ml) was added and stirring continued (2.5 h) at 20 °C. The product was washed with water, the dried (MgSO$_4$) ether layer evaporated, and the crude product (965 mg) chromatographed on silica (40 g); elution with petroleum gave $(+)$-1,3-$dimethyl$-1-Z-$styrylindene$ (125 mg) as an oil (Found: M^+, 246.140 6. $C_{19}H_{18}$ requires M, 246.140 8); $\nu_{max.}$ 1 603 and 1 381 cm^{-1}; τ(60 MHz) 2.95 (9 H, m, aromatic), 3.57 (1 H, d, J 12 Hz), 4.08 (1 H, d, J 12 Hz), 4.24 (1 H, q, J 1.5 Hz), 8.12 (3 H, d, J 1.5 Hz), and 8.69 (3 H, s); $[\alpha]_D^{24}$ $+393°$ (c 0.866, CHCl$_3$).

Continued elution of the column gave $(+)$-1,3-$dimethyl$-1-E-$styrylindene$ (220 mg) as an oil (Found: M^+, 246.140 8); $\nu_{max.}$ 1 640, 1 600, 1 381, and 968 cm^{-1}; τ(60 MHz) 2.71 (9 H, m, aromatic), 3.47 (1 H, d, J 16 Hz), 3.82 (1 H, d, J 16 Hz), 3.94 (1 H, q, J 1.5 Hz), 7.90 (3 H, d, J 1.5 Hz), and 8.52 (3 H, s); $[\alpha]_D^{24}$ $+290.5°$ (c 0.811, CHCl$_3$).

$(+)$-1,3-$Dimethyl$-1-Z-p-$nitrostyrylindene$ and $(+)$-1,3-Di-$methyl$-1-E-p-$nitrostyrylindene$.—Butyl-lithium (352 mg, 5.5 mmol) in hexane (2.25 ml) was added by syringe to a stirred slurry of p-nitrobenzyltriphenylphosphonium chloride (2.44 g, 5.6 mmol) in tetrahydrofuran (50 ml) at 20 °C under nitrogen. After stirring (2 h) at 20 °C, 1-formyl-1,3-dimethylindene[2] (470 mg, 2.74 mmol) in tetrahydrofuran (5 ml) was added, and the suspension stirred at 40 °C (21 h). The product was washed with water, the dried (MgSO$_4$) ether layer evaporated, and the product (1.45 g) chromatographed on silica (70 g). Elution with benzene gave an impure mixture of the styrylindenes (334 mg) and recovered starting material (300 mg). The mixture of styrylindenes was chromatographed on silica (35 g); elution with benzene–petroleum (1 : 4) gave the Z-isomer (248 mg) contaminated with p-nitrotoluene which was removed by steam distillation to give $(+)$-1,3-$dimethyl$-1-Z-p-$nitrostyrylindene$

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* For alternative TS arrangements see refs. 2 and 22. Although description of the TS in terms of interacting radicals is useful for the cyclopentadiene system (ref. 8) its use for the indene system is avoided as the HOMO of the indene radical is nodal at C-2.

(170 mg) as yellow plates, m.p. 67—71 °C (from petroleum, b.p. 40—60 °C) (Found: M^+, 291.125 8. $C_{19}H_{17}NO_2$ requires M, 291.125 9); $\nu_{max.}$ (Nujol) 1 637, 1 595, and 1 107 cm^{-1}; $\lambda_{max.}$ (EtOH) 263 and 295 nm (ε 11 200 and 8 860); τ(60 MHz) 2.20 (2 H, m, aromatic), 2.91 (4 H, m, aromatic), 3.27 (2 H, m, aromatic), 3.62 (1 H, d, J 12 Hz), 3.89 (1 H, d, J 12 Hz), 4.21 (1 H, q, J 1.5 Hz), 8.10 (3 H, d, J 1.5 Hz), and 8.66 (3 H, s); $[\alpha]_D^{24}$ +453.5° (c 0.781, CHCl$_3$).

Continued elution of the column gave (+)-1,3-*dimethyl-1-E-p-nitrostyrylindene* (60 mg) as a yellow oil (Found: M^+, 291.125 8); $\nu_{max.}$ 1 639, 1 596, 1 342, and 1 109 cm^{-1}; $\lambda_{max.}$ (EtOH) 327 and 260 (sh) nm (ε 15 400 and 9 140); τ(60 MHz) 1.88 (2 H, m, aromatic), 2.58 (2 H, m, aromatic), 2.71 (4 H, s, aromatic), 3.44 (1 H, d, J 16 Hz), 3.67 (1 H, d, J 16 Hz), 3.96 (1 H, q, J 1.5 Hz), 7.86 (3 H, d, J 1.5 Hz), and 8.50 (3 H, s); $[\alpha]_D^{24}$ +328° (c 1.066, CHCl$_3$).

Mixture of 1,3-Dimethyl-2-E-propenylindene and 1,3-Dimethyl-2-Z-propenylindene.—Butyl-lithium (52.2 mg, 0.82 mmol) in hexane (0.65 ml) was added by syringe to a stirred slurry of ethyltriphenylphosphonium bromide (310 mg, 0.835 mmol) in ether (8 ml) at 0 °C under nitrogen. After stirring at 0 °C (2 h), 2-formyl-1,3-dimethylindene [2] (100 mg, 0.582 mmol) in ether (2 ml) was added and stirring continued at 0° (100 min) and 20 °C (60 min). The product was washed with water, and the ether layer was dried (MgSO$_4$) and evaporated to give a crude product (177 mg), which was chromatographed on silica (32 g) in benzene–petroleum to give an inseparable mixture (t.l.c.) of E- and Z-1,3-dimethyl-2-propenylindene (75 mg, 70%). This mixture was compared by n.m.r., i.r., and t.l.c. with the products of thermolysis of 1,3-dimethyl-2-Z-propenylindene and its E-isomer (see below).

(+)-1-E-*Ethoxycarbonylvinyl-1,3-dimethylindene.*— Sodium hydride (50% dispersion in paraffin, 462 mg, 9.62 mmol) in 1,2-dimethoxyethane (15 ml) was stirred under nitrogen at 0—5 °C and triethyl phosphonoacetate (2.23 g, 9.95 mmol) in 1,2-dimethoxyethane (30 ml) added. After stirring at 20 °C (1 h), (+)-1-formyl-1,3-dimethylindene [2] (1.42 g, 8.25 mmol) in 1,2-dimethoxyethane (15 ml) was added, and the mixture stirred at 20 °C (30 min). The product was diluted with ether, and the organic layer washed with water, dried (MgSO$_4$), and evaporated. The crude product (2.14 g) was chromatographed on silica (120 g); elution with benzene gave (+)-1-E-*ethoxycarbonylvinyl-1,3-dimethylindene* (1.70 g, 85%) as an oil (Found: M^+, 242.130 1. $C_{16}H_{18}O_2$ requires M, 242.130 7); $\nu_{max.}$ 1 718 and 1 643 cm^{-1}; $\lambda_{max.}$ (EtOH) 253, 285 (sh) and 294 (sh) nm (ε 9 853, 3 637, and 2 464); τ(60 MHz) 2.76 (4 H, m, aromatic), 3.18 (1 H, d, J 16 Hz), 4.03 (1 H, d, J 16 Hz), 4.04 (1 H, q, J 1.5 Hz), 5.88 (2 H, q, J 7 Hz), 7.91 (3 H, d, J 1.5 Hz), 8.59 (3 H, s), and 8.80 (3 H, t, J 7 Hz); $[\alpha]_D^{24}$ +153.2° (c 1.22, CHCl$_3$).

(+)-1-E-*Hydroxymethylvinyl-1,3-dimethylindene.*—A solution of lithium aluminium monoethoxyhydride was prepared [10] from lithium aluminium hydride (950 mg) and absolute alcohol (1.15 g) in ether (40 ml) and the product made up to 100 ml with ether. This solution (20 ml) was added in four portions during 5 min to (+)-1-E-ethoxycarbonylvinyl-1,3-dimethylindene (1.224 g) in ether (70 ml) with stirring under nitrogen at 0 °C. After stirring at 0 °C (30 min), water was added and the ether layer washed with water, dried (MgSO$_4$), and evaporated. The crude product (1.05 g) was chromatographed on silica (100 g); elution with ether–benzene (1 : 4) gave (+)-1-E-*hydroxymethylvinyl-1,3-dimethylindene* (374 mg, 37%) as an oil

(Found: M^+, 200.119 4. $C_{14}H_{16}O$ requires M, 200.120 1); $\nu_{max.}$ 3 340 cm^{-1}; τ(60 MHz) 2.79 (4 H, m, aromatic), 4.02 (1 H, q, J 1.5 Hz), 4.34 (2 H, m, olefinic), 6.03 (2 H, broadened inner lines of AB-system), 7.78 (1 H, br s, OH), 7.93 (3 H, d, J 1.5 Hz), and 8.66 (3 H, s); $[\alpha]_D^{24}$ +94.8° (c 1.10, CHCl$_3$).

(+)-1-E-*Formylvinyl-1,3-dimethylindene.*—The foregoing alcohol (400 mg, 2.0 mmol) was oxidised during 15 min with chromium trioxide (1.2 g, 12 mmol) and pyridine (1.9 g, 24 mmol) in dichloromethane (50 ml), and the reaction worked-up in the usual way. The crude product (350 mg) was chromatographed on silica (40 g); elution with benzene gave (+)-1-E-*formylvinyl-1,3-dimethylindene* (312 mg, 79%) as an oil (Found: M^+, 198.104 0. $C_{14}H_{14}O$ requires M, 198.104 4); $\nu_{max.}$ 1 687 and 1 625 cm^{-1}; $\lambda_{max.}$ 258 (sh), 287 (sh), and 296 nm (ε 9 057, 3 748, and 3 383); τ(60 MHz) 0.56 (1 H, d, J 7 Hz, CHO), 2.77 (4 H, m, aromatic), 3.48 (1 H, d, J 16 Hz), 3.79 (1 H, dd, J 16 and 7 Hz), 4.07 (1 H, q, J 1.5 Hz), 7.92 (3 H, d, J 1.5 Hz), and 8.59 (3 H, s); $[\alpha]_D^{24}$ +132.0° (c 1.20, CHCl$_3$).

(−)-1-E-*Carboxyvinyl-1,3-dimethylindene.* (−)-1-E-Ethoxycarbonylvinyl-1,3-dimethylindene was prepared as described above for the preparation of the (+)-isomer, from (−)-1-formyl-1,3-dimethylindene (1 g). The crude unchromatographed product was stirred with ethanol (15 ml) and 2M sodium hydroxide solution (15 ml) (18 h). After acidification (H$_2$SO$_4$) the product was evaporated to remove ethanol and the residue diluted with water and extracted with ether. Extraction of the ether layer with portions of saturated sodium hydrogen carbonate solution, acidification and ether extraction of the aqueous extracts, drying (MgSO$_4$), and evaporation of the ether extract gave (−)-(1)-E-*carboxyvinyl-1,3-dimethylindene* (0.97 g) (Found: M^+, 214.099 2. $C_{14}H_{14}O_2$ requires M, 214.099 4); $\nu_{max.}$ 2 200—3 400, 1 690, and 1 640 cm^{-1}; τ(60 MHz) −0.5 (br, 1 H), 2.72 (4 H, s, aromatic), 3.05 (1 H, d, J 16 Hz), 4.05 (1 H, d, J 16 Hz), 4.05 (1 H, q, J 1.5 Hz), 7.9 (3 H, d, J 1.5 Hz), and 8.58 (3 H, s). With diazomethane in ether–methanol the acid gave the methyl ester as an oil; τ(60 MHz) 2.83 (4 H, m, aromatic), 3.17 (1 H, d, J 16 Hz), 4.1 (1 H, d, J 16 Hz), 4.1 (1 H, q, J 1.5 Hz), 6.44 (3 H, s), 7.98 (3 H, d, J 1.5 Hz), and 8.65 (3 H, s).

(−)-1,3-*Dimethyl-1-E-phenoxycarbonylvinylindene.*— The foregoing acid (120 mg) and oxalyl chloride (2 ml) were stirred at 20 °C (2 h). Removal of oxalyl chloride under reduced pressure gave the acid chloride; τ 2.75 (4 H, m, aromatic), 3.03 (1 H, d, J 15 Hz), 3.86 (1 H, d, J 15 Hz), 4.06 (1 H, q, J 1.5 Hz), 7.88 (3 H, d, J 1.5 Hz), and 8.56 (3 H, s). This product, 1,2-dimethoxyethane (10 ml), and sodium phenoxide (100 mg) were stirred at 20 °C (2 h) and the mixture refluxed (1 h). Chromatography over silica in benzene gave (−)-1,3-*dimethyl-1-E-phenoxycarbonylvinylindene* (45 mg) (Found: M^+, 290.131 2. $C_{20}H_{18}O_2$ requires M, 290.130 7); τ(60 MHz) 2.7 (4 H, m, aromatic), 2.98 (1 H, d, J 15 Hz), 3.87 (1 H, d, J 15 Hz), 4.0 (1 H, q, J 1.5 Hz), 7.86 (3 H, d, J 1.5 Hz), and 8.5 (3 H, s); $[\alpha]_D^{24}$ −196.6° (c 2.36, CHCl$_3$).

(−)-1,3-*Dimethyl-1-E-methylaminocarbonylvinylindene.*— The acid chloride prepared from (−)-1-E-carboxyvinyl-1,3-dimethylindene (50 mg) as described above was dissolved in benzene (2 ml), and methylamine gas bubbled into the solution (5 min). The product was diluted with dichloromethane and the organic layer washed successively with water, dilute hydrochloric acid, and saturated sodium hydrogen carbonate solution, dried (MgSO$_4$), and evaporated.

Chromatography of the product on silica in chloroform–methanol (49 : 1) gave (−)-1,3-*dimethyl*-1-E-*methylaminocarbonylvinylindene* (22 mg) (Found: M^+, 227.129 9. $C_{15}H_{17}NO$ requires M, 227.131 0); τ(60 MHz) 2.79 (4 H, m, aromatic), 3.27 (1 H, d, J 16 Hz), 4.08 (1 H, q, J 1.5 Hz), 4.22 (1 H, d, J 16 Hz), 7.22 [3 H, d (?), J 5 Hz], 7.9 (3 H, d, J 1.5 Hz), and 8.6 (3 H, s).

(−)-1-E-*Acetylvinyl*-1,3-*dimethylindene*.— (−)-1-*E*-Formylvinyl-1,3-dimethylindene (100 mg) in ether (2 ml) was treated with methylmagnesium iodide [1.5 ml of a solution from magnesium (0.121 g) and methyl iodide (1.42 g) in ether (10 ml)] at 20 °C (30 min). The product was diluted with ether and the organic phase washed with ammonium chloride solution, and then water, dried (MgSO₄), and evaporated to give the alcohol (125 mg). Without purification this alcohol (125 mg) was oxidised with CrO₃–pyridine [CrO₃ (0.346 g), pyridine (0.554 g), in dichloromethane (30 ml)] over 30 min. Work-up in the usual way gave the crude ketone (110 mg) which was chromatographed on silica in benzene–ether (95 : 5) to give (−)-1-E-*acetylvinyl*-1,3-*dimethylindene* (100 mg) (Found: M^+, 212.119 3. $C_{15}H_{16}O$ requires M^+, 212.120 1); $\nu_{max.}$ 1 690, 1 670, and 1 610 cm⁻¹; τ 2.79 (4 H, m, aromatic), 3.42 (1 H, d, J 16 Hz), 3.85 (1 H, d, J 16 Hz), 4.08 (1 H, q, J 1.5 Hz), 7.86 (3 H, s), 7.87 (3 H, d, J 1.5 Hz), and 8.59 (3 H, s).

(−)-1-E-*Benzoylvinyl*-1,3-*dimethylindene*.— (−)-1-*E*-Formylvinyl-1,3-dimethylindene (100 mg) in ether (3 ml) was treated with phenylmagnesium bromide [1.5 ml of a solution from magnesium (121.2 mg) and bromobenzene (793 mg) in ether (10 ml)] at 20 °C (30 min). The product was diluted with ether and the organic phase washed with ammonium chloride solution and then water, dried (MgSO₄), and evaporated to give a crude product (110 mg) which was oxidised with CrO₃–pyridine [from chromium trioxide (0.346 g) and pyridine (0.554 g) in dichloromethane (30 ml)] at 20 °C (30 min). Work-up in the usual way and chromatography on silica in benzene gave (−)-1-E-*benzoylvinyl*-1,3-*dimethylindene* (50 mg) (Found: M^+, 274.135 3. $C_{20}H_{18}O$ requires M, 274.135 7); $\nu_{max.}$ 1 665, 1 643, 1 609, and 1 578 cm⁻¹; τ 2.15 (2 H, m, aromatic), 2.42—2.85 (7 H, m, aromatic), 3.09 (2 H, s, olefinic), 3.99 (1 H, q, J 1.5 Hz), 7.89 (3 H, d, J 1.5 Hz), and 8.5 (3 H, s).

(+)-1-Z-*Cyanovinyl*-1,3-*dimethylindene* and (+)-1-E-*Cyanovinyl*-1,3-*dimethylindene*.—Sodium hydride (50% dispersion in paraffin, 101 mg, 2.1 mmol) in 1,2-dimethoxyethane (5 ml) was stirred under nitrogen at 0—5 °C and diethyl cyanomethylphosphonate (359 mg, 2.03 mmol) in 1,2-dimethoxyethane (5 ml) was added. After stirring at 20 °C (1 h), (+)-1-formyl-1,3-dimethylindene [2] (250 mg, 1.45 mmol) in 1,2-dimethoxyethane (5 ml) was added, and the mixture stirred at 20 °C (30 min). The product was diluted with ether, and the organic layer washed with water, dried (MgSO₄), and evaporated to give the crude product (331 mg), which was chromatographed on silica (30 g); elution with benzene–petroleum (1 : 1) gave a mixture (257 mg) of Z- and E-cyanovinylindenes, which was chromatographed on 20% silver nitrate–silica (50 g) in benzene. Elution with benzene gave (+)-1-E-*cyanovinyl*-1,3-*dimethylindene* (196 mg, 69%) as an oil (Found: M^+, 195.104 0. $C_{14}H_{13}N$ requires M, 195.104 8); $\nu_{max.}$ 2 220 and 1 618 cm⁻¹; τ(60 MHz) 2.5—2.9 (4 H, m), 3.44 (1 H, d, J 16 Hz), 4.08 (1 H, m, olefinic), 4.57 (1 H, d, J 16 Hz), 7.90 (3 H, d, J 1.5 Hz), and 8.61 (3 H, s); $[\alpha]_D^{24}$ +218° (c 1.04, CHCl₃).

Continued elution of the column gave (+)-1-Z-*cyanovinyl*-1,3-*dimethylindene* (36 mg, 13%) as an oil (Found: M^+, 195.104 0); $\nu_{max.}$ 2 220 and 1 620 cm⁻¹; τ(60 MHz) 2.68 (4 H, m), 3.69 (1 H, d, J 12 Hz), 3.74 (1 H, m, olefinic), 4.73 (1 H, d, J 12 Hz), 7.85 (3 H, d, J 1.5 Hz), and 8.38 (3 H, s); $[\alpha]_D^{24}$ +84.7° (c 0.562, CHCl₃).

(+)-1,3-*Dimethyl*-1-*isopropenylindene*.— Butyl-lithium (120 mg, 1.88 mmol) in hexane (0.8 ml) was added by syringe to a stirred slurry of methyltriphenylphosphonium bromide (790 mg, 2.21 mmol) in ether (50 ml) at 20 °C under nitrogen, and the mixture stirred at 20 °C (2 h). (+)-1-Acetyl-1,3-dimethylindene [2] (197 mg, 1.06 mmol) in ether (10 ml) was then added and stirring continued at 20 °C (90 min). The product was washed with water, and the ether layer dried (MgSO₄) and evaporated to give a product (414 mg) which was chromatographed on silica in petroleum to give a 1 : 1 mixture (110 mg) of the required product and 1,3-dimethylindene. Butyl-lithium (30 mg) in hexane (0.2 ml) was added with stirring to the mixture (110 mg) in ether (15 ml) at 20 °C under nitrogen, and after 30 min the reaction mixture was poured onto a slurry of solid carbon dioxide–ether. After reaching room temperature the ether solution was washed with saturated sodium hydrogen carbonate solution, washed with water, dried (MgSO₄), and evaporated. The crude product (79 mg) was chromatographed on silica; elution with petroleum gave (+)-1,3-*dimethyl*-1-*isopropenylindene* (40 mg, 20%) as an oil (Found: M^+, 184.125 2. $C_{14}H_{16}$ requires M, 184.125 2); $\nu_{max.}$ 1 638 cm⁻¹; τ(60 MHz) 2.75 (4 H, m), 4.01 (1 H, q, J 1.5 Hz), 4.89 (1 H, m, olefinic), 5.07 (1 H, m, olefinic), 7.86 (3 H, d, J 1.5 Hz), 8.58 (3 H, s), and 8.61 (3 H, m); $[\alpha]_D^{24}$ +21.4° (c 1.52, CHCl₃).

Preparative Thermolysis of 1-Vinylindenes.—(i) (+)-1,3-Dimethyl-1-*Z*-propenylindene (95 mg) and 1,2,4-trichlorobenzene (1 ml) were refluxed (213 °C) under nitrogen (10 h). The n.m.r. spectrum indicated conversion to a mixture of *Z*- and E-2-propenylindenes which was not separable by t.l.c.; the mixture was therefore heated at 213 °C (36 h) to complete conversion to the *E*-2-propenylindene. Chromatography of the product on silica (30 g) in petroleum gave 1,3-*dimethyl*-2-E-*propenylindene* (16 mg) as an oil (Found: M^+, 184.125 2); $\nu_{max.}$ 1 660, 1 601, 1 468, and 961 cm⁻¹; τ(60 MHz), 2.73 (4 H, m), 3.49 (1 H, dq, J 16 and 1 Hz), 4.18 (1 H, dq, J 16 and 7 Hz), 6.49 (1 H, qq, J 7.5 and 1.5 Hz), 7.88 (3 H, d, J 1.5 Hz), 8.07 (3 H, dd, J 7 and 1 Hz), and 8.69 (3 H, d, J 7.5 Hz).

(ii) (+)-1,3-Dimethyl-1-*E*-propenylindene (30 mg) was refluxed with 1,2,4-trichlorobenzene (1 ml) (74 h) under nitrogen, and starting material (4 mg) and 1,3-dimethyl-2-*E*-propenylindene (16 mg) isolated by chromatography on silica in petroleum.

(iii) (+)-1,3-Dimethyl-1-*E*-styrylindene (71 mg) was refluxed in 1,2,4-trichlorobenzene (5 ml) under nitrogen (17 h). Removal of solvent under reduced pressure gave 1,3-*dimethyl*-2-E-*styryl*-1,3-*dimethylindene* (63 mg, 89%), m.p. 50—53 °C (from methanol) (Found: C, 92.4; H, 7.5. $C_{19}H_{18}$ requires C, 92.7; H, 7.3%); $\nu_{max.}$ (Nujol) 1 619, 1 597, 1 448, and 953 cm⁻¹; $\lambda_{max.}$ (EtOH) 241, 259, 330, 344, and 356 nm (ε 12 500, 7 200, 33 100, 41 200, and 28 300); τ(60 MHz) 2.68 (10 H, m, aromatic and olefinic), 3.33 (1 H, d, J 16 Hz), 6.32 (1 H, qq, J 8 and 1.5 Hz), 7.79 (3 H, d, J 1.5 Hz), and 8.62 (3 H, d, J 8 Hz).

(iv) (+)-1,3-Dimethyl-1-*Z*-styrylindene (72 mg) and phenetole (3 ml) were refluxed (171 °C) for 23 h. Evaporation of solvent at 100 °C *in vacuo* and chromatography on silica in petroleum gave 1,3-*dimethyl*-2-Z-*styrylindene* (53

mg) as a colourless oil (Found: M^+, 246.140 6. $C_{19}H_{18}$ requires M, 246.140 8), $\nu_{max.}$ 1 605, 1 455, and 1 020 cm^{-1}; $\lambda_{max.}$ 238 and 316 nm (ε 14 100 and 13 600); τ(60 MHz) 2.74 (9 H, m, aromatic), 3.37 (1 H, d, J 12 Hz), 3.57 (1 H, d, J 12 Hz), 6.50 (1 H, qq, J 8 and 1.5 Hz), 8.09 (3 H, d, J 1.5 Hz), and 8.87 (3 H, d, J 8 Hz). To determine the stereo-specificity of the rearrangement of 1,3-dimethyl-1-Z-styrylindene to the 2-isomer, the former compound (80 mg) in 1,2,4-trichlorobenzene (0.5 ml) containing a little trioxan as internal standard was degassed (five freeze-thaw cycles) and sealed in an n.m.r. tube. The tube was heated at 180 °C (constant-temperature bath) and the progress of the reaction noted by n.m.r. examination after 18 960, 32 700, and 50 400 s. The product mixture was chromato-graphed on silica in petroleum to give 1,3-dimethyl-2-Z-styrylindene (39 mg). This was sealed in an n.m.r. tube as above and heated at 180 °C. The tube was periodically cooled and examined by n.m.r. to obtain a rate for the conversion of the 2-Z-styrylindene into the E-isomer. The rate constant for disappearance of the 1-Z-styrylindene (k_1) was found to be 5.41 × 10^{-5} s^{-1}, and the rate constant for conversion of the 2-Z-styrylindene to its E-isomer (k_2) was 1.495 × 10^{-5} s^{-1}.

(*v*) 1,3-Dimethyl-1-E-p-nitrostyrylindene (35 mg) and decalin (3 ml) were refluxed (190 °C) under nitrogen for 20 h. The solvent was removed at 100 °C *in vacuo* and the crude product chromatographed on silica; elution with benzene–petroleum (3 : 7) gave 1,3-*dimethyl*-2-E-p-*nitro-styrylindene* (26 mg) as orange plates, m.p. 142—145 °C [from benzene–light petroleum (b.p. 40—60 °C)] (Found: C, 78.5; H, 6.1; N, 4.7. $C_{19}H_{17}NO_2$ requires C, 78.4; H, 5.8; N, 4.8%); $\nu_{max.}$ (Nujol) 1 615, 1 581, 1 497, and 1 108 cm^{-1}; $\lambda_{max.}$ (EtOH) 257, 305, and 405 nm (ε 10 400, 9 424, and 31 521), τ(60 MHz) 1.78 (2 H, m, aromatic), 2.38 (2 H, m, aromatic), 2.62 (5 H, m, aromatic and olefinic), 3.31 (1 H, d, J 16 Hz), 6.30 (1 H, qq, J 7.5 and 1.5 Hz), 7.70 (3 H, d, J 1.5 Hz), and 8.57 (3 H, d, J 7.5 Hz).

(*vi*) 1,3-Dimethyl-1-Z-p-nitrostyrylindene (35 mg) in cumene (3 ml) was refluxed (152 °C) under nitrogen for 23 h. The solvent was removed at 100 °C *in vacuo* and the product (43 mg) chromatographed on silica in benzene–petroleum (1 : 4) to give a mixture (25 mg) of 1,3-dimethyl-2-Z-p-nitrostyrylindene and its E-isomer, ratio 3 : 1 by n.m.r. spectroscopy.

(*vii*) 1-E-Ethoxycarbonylvinyl-1,3-dimethylindene (100 mg) and decalin (3 ml) were refluxed (190 °C) under nitrogen for 30 h. The solvent was removed at 100 °C *in vacuo* and the product chromatographed on silica in benzene–petroleum (4 : 1) to give 2-E-*ethoxycarbonylvinyl*-1,3-*dime-thylindene* (72 mg, 72%) as a pale yellow oil (Found: M^+, 242.131 1. $C_{16}H_{18}O_2$ requires M, 242.130 7); $\nu_{max.}$ 1 709 and 1 615 cm^{-1}; $\lambda_{max.}$ (EtOH) 237 (sh), 246, 253.5, and 338 nm (ε 5 381, 7 567, 6 727, and 26 570); τ(60 MHz) 2.16 (1 H, d, J 16 Hz), 2.64 (4 H, m, aromatic), 4.03 (1 H, d, J 16 Hz), 5.74 (2 H, q, J 7 Hz), 6.42 (1 H, qq, J 8 and 1.5 Hz), 7.73 (3 H, d, J 1.5 Hz), 8.66 (3 H, t, J 7 Hz), and 8.67 (3 H, d, J 8 Hz).

(*viii*) (+)-1-E-Formylvinyl-1,3-dimethylindene (100 mg) and phenetole (3 ml) were refluxed (171 °C) under nitrogen for 22 h. The solvent was removed at 100 °C *in vacuo* and the product chromatographed on silica in benzene to give 2-E-*formylvinyl*-1,3-*dimethylindene* (79 mg, 79%) as yellow plates, m.p. 78—80 °C (from petroleum) (Found: C, 84.95; H, 7.0. $C_{14}H_{14}O$ requires C, 84.8; H, 7.1%); $\nu_{max.}$ 1 670 and 1 598 cm^{-1}; $\lambda_{max.}$ (EtOH) 230, 249, 256.5, and 353 nm

(ε 5 500, 7 250, 7 000, and 30 000); τ(60 MHz) 0.32 (1 H, d, J 8 Hz, CHO), 2.42 (1 H, d, J 16 Hz), 2.62 (4 H, m, aromatic), 3.76 (1 H, dd, J 16 and 8 Hz), 6.39 (1 H, qq, J 8 and 1.5 Hz), 7.69 (3 H, d, J 1.5 Hz), and 8.66 (3 H, d, J 8 Hz).

(*ix*) 1-E-Cyanovinyl-1,3-dimethylindene (90 mg) and decalin (3 ml) were refluxed (190 °C) under nitrogen for 23 h. Removal of solvent at 100 °C *in vacuo* gave a product which was chromatographed on silica in benzene–petroleum (7 : 3) to give 2-E-*cyanovinyl*-1,3-*dimethylindene* (74 mg, 82%), m.p. 86—89 °C (from petroleum) (Found: C, 85.85; H, 6.5; N, 6.85. $C_{14}H_{13}N$ requires C, 86.15; H, 6.7; N, 7.2%); $\nu_{max.}$ 2 210 and 1 598 cm^{-1}; $\lambda_{max.}$ (EtOH) 239 (sh), 246, 254, and 336 nm (ε 6 986, 9 180, 7 984, and 30 140); τ(60 MHz) 2.50 (1 H, d, J 16 Hz), 2.62 (4 H, m, aromatic), 4.69 (1 H, d, J 16 Hz), 6.48 (1 H, qq, J 7 and 1.5 Hz), 7.78 (3 H, d, J 1.5 Hz), and 8.69 (3 H, d, J 7 Hz).

(*x*) 1-Z-Cyanovinyl-1,3-dimethylindene (20 mg) and decalin (0.5 ml) were degassed (three freeze-thaw cycles) in an n.m.r. tube, and heated at 150 °C (68 h). The tube was opened, and solvent removed at 100 °C *in vacuo*. The n.m.r. spectrum of the product indicated a mixture of 2-E-cyanovinyl-1,3-dimethylindene and 2-Z-cyanovinyl-1,3-di-methylindene in the ratio 1 : 3; τ(90 MHz) 2.62 (4 H, m, aromatic), 2.79 (1 H, d, J 12 Hz), 4.73 (1 H, d, J 12 Hz), 5.73 (1 H, m), 7.73 (3 H, d, J 1.5 Hz), and 8.57 (3 H, d, J 7 Hz).

(*xi*) 1,3-Dimethyl-1-E-phenoxycarbonylvinylindene (47 mg) was heated in diphenyl ether at 180 °C for 22 h. The product was chromatographed on silica in benzene to give 1,3-*dimethyl*-2-E-*phenoxycarbonylvinylindene* (30 mg) (Found: M^+, 290.130 1. $C_{20}H_{18}O_2$ requires M, 290.130 7); τ(60 MHz) 1.98 (1 H, d, J 16 Hz), 2.7 (9 H, m, aromatic), 3.88 (1 H, d, J 16 Hz), 6.35 (1 H, qq, J 7 and 1.5 Hz), 7.7 (3 H, d, J 1.5 Hz), and 8.61 (3 H, d, J 7 Hz).

(*xii*) 1-E-Acetylvinyl-1,3-dimethylindene (50 mg) was heated in diphenyl ether (2 ml) at 190 °C (24 h) and the product chromatographed on silica in benzene–ether (1 : 1) to give 2-E-*acetylvinyl*-1,3-*dimethylindene* (15 mg), m.p. 85—88 °C (from petroleum) (Found: C, 84.7; H, 7.4%; M^+, 212.120 4. $C_{15}H_{16}O$ requires C, 84.9; H, 7.6%; M, 212.120 1); τ(60 MHz) 2.34 (1 H, d, J 16 Hz), 2.68 (4 H, m, m, aromatic), 3.78 (1 H, d, J 16 Hz), 6.42 (1 H, qq, J 7 and 1.5 Hz), 7.66 (3 H, s), 7.72 (3 H, d, J 1.5 Hz), 8.68 (3 H, d, J 7 Hz).

(*xiii*) 1-E-Benzoylvinyl-1,3-dimethylindene (49 mg) in diphenyl ether (2 ml) was heated at 180 °C (24 h). Chro-matography of the product on silica in benzene gave 2-E-*benzoylvinyl*-1,3-*dimethylindene* (20 mg) (Found: M^+, 274.134 8. $C_{20}H_{18}O$ requires M, 274.135 8); $\nu_{max.}$ 1 650, 1 598, and 1 570 cm^{-1}; τ(90 MHz) 1.95 (1 H, d, J 16 Hz), 1.95 (2 H, m, aromatic), 2.55 (7 H, m, aromatic), 2.94 (1 H, d, J 16 Hz), 6.26 (1 H, qq, J 7 and 1.5 Hz), 7.67 (3 H, d, J 1.5 Hz), and 8.56 (3 H, d, J 7 Hz).

(*xiv*) (−)-1-E-Carboxyvinyl-1,3-dimethylindene (50 mg) was converted into the acid chloride as previously described and the latter heated in boiling xylene (2 h). The n.m.r. spectrum of the product obtained by evaporation of xylene under reduced pressure indicated fairly pure acid chloride, which was stirred with ethanol (2 ml) and calcium carbonate (0.4 g) (18 h). Chromatography of the product on silica in benzene gave the pure ethyl ester (29 mg), $[\alpha]_D^{24}$ −131.7° (*c* 1.45 CHCl$_3$) indicating 14% loss of optical activity) ($k_{rac.}$ 2.1 × 10^{-5} s^{-1} at 140 °C). Repetition of the experi-ment but heating the acid chloride for 4 h in boiling xylene

resulted in an optical activity loss of 24.3% and a racemisation rate constant of 1.92×10^{-5} s^{-1} at 140 °C.

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