

## *o*-Quinonoid Compounds. Part 14.<sup>1</sup> 1,5-Acyl Shifts in Substituted Indenes: Migratory Aptitudes from Racemisation Rates

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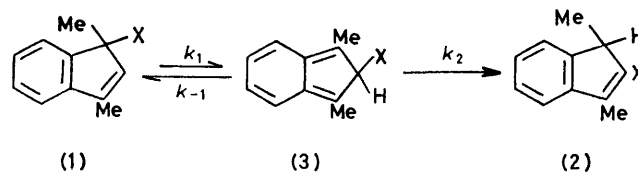
Racemisation rates for the indenenes (1) provide migratory aptitudes for acyl, vinyl, ethynyl, nitrile, and alkyl groups, as well as hydrogen. Migratory aptitude decreases in the order: HCO > Bz ~ Ac > H > vinyl > CONHMe > CO<sub>2</sub>Ph > CO<sub>2</sub>Me > CN ~ C≡CH > alkyl. It is suggested that a similar order may apply to all 1,5-sigmatropic shifts. It is proposed that the fast migration of formyl, acetyl, and benzoyl groups is, at least in part, due to a secondary interaction involving the carbonyl π\* orbital. Small substituent effects on the rearrangement of the *p*-substituted benzoylindenenes, and small solvent rate effects suggest little increased polarity in the rearrangement transition states. Racemisation of (1; X = Ac) and (1; X = Bz) is accelerated in the presence of boron trifluoride-ether.

ALTHOUGH considerable progress has been made in understanding substituent effects in cycloaddition reactions,<sup>2</sup> large substituent effects in electrocyclic and sigmatropic processes are less well understood.<sup>3</sup> For the 1,5-sigmatropic shift the fast migration of unsaturated groups (acyl,<sup>1,4a,b</sup> aryl,<sup>4c</sup> butadienyl,<sup>4d</sup> and vinyl<sup>4e</sup>) compared to alkyl groups is striking. The work described in this paper was undertaken in an attempt to substantiate our early suggestion<sup>5a</sup> that this migratory aptitude difference arose as a result of homoconjugative interaction between the π-systems of the diene and migrating unsaturated group. This view was refined in our preliminary communication<sup>5b</sup> and subsequently independently suggested by others.<sup>5c</sup>

We showed<sup>1</sup> that a variety of 1-acyl-1,3-dimethylindenenes (1; X = acyl) rearranged thermally to 2-acyl-1,3-dimethylindenenes (2; X = acyl), and on the basis of trapping experiments and other evidence proposed a mechanism for the rearrangement (Scheme) involving 1,5-sigmatropic shift to a 2*H*-indene intermediate (3; X = acyl) followed by a 1,5-hydrogen shift giving the 2-acylindene. It had been our intention to use the overall rates of conversion of 1-acyl- (1) into 2-acylindenenes (2) as measures of the migratory aptitudes of different acyl groups X. However, this approach was confounded when orienting experiments<sup>1</sup> showed that for X = CHO, Ac, and Bz, reverse acyl shift in the 2*H*-indenenes (3) is more rapid than the hydrogen shift leading to the 2-acylindenenes (2). At the same time these studies<sup>1</sup> revealed marked migratory aptitude differences for the different acyl groups. To obtain quantitative migratory aptitude data for acyl and other groups we sought to prepare the indenenes (1) in optically active form; 1,5-acyl shift would give the symmetric iso-

indenenes (3) with loss of optical activity. With optically active substrates certain stringent tests for concertedness of the 1,5-acyl shift would also be possible.<sup>4b</sup>

*Preparation of Optically Active Indenenes.*—1,3-Dimethylindene-1-carboxylic acid (1; X = CO<sub>2</sub>H), prepared by pouring 1,3-dimethylindenyl-lithium over solid carbon dioxide,<sup>1</sup> was readily resolved by crystallisation of the quinine salt. Reduction (LiAlH<sub>4</sub>, -20 °C) of the acid to the alcohol (1; X = CH<sub>2</sub>OH) and oxidation of the latter (CrO<sub>3</sub>-C<sub>5</sub>H<sub>5</sub>N-CH<sub>2</sub>Cl<sub>2</sub>) to the (+)-aldehyde



SCHEME

(1; X = CHO) were carried out as described for the corresponding racemic compounds.<sup>1</sup> The (+)-aldehyde was converted into a range of optically active 1-acylindenenes by Grignard additions followed by oxidation (CrO<sub>3</sub>-C<sub>5</sub>H<sub>5</sub>N-CH<sub>2</sub>Cl<sub>2</sub>). In addition to the compounds whose preparation in racemic form has already been described<sup>1</sup> the (+)-ketone (1; X = COC<sub>6</sub>H<sub>4</sub>OMe-*p*) was prepared in this way and the (+)-sulphone (1; X = COC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Me-*p*) was obtained by addition of the Grignard reagent from *p*-bromothioanisole to (1; X = CHO) and oxidation of the resulting alcohol first with CrO<sub>3</sub>-C<sub>5</sub>H<sub>5</sub>N-CH<sub>2</sub>Cl<sub>2</sub> and then with periodic acid. Wittig reaction between the (+)-aldehyde and methylenetriphenylphosphorane gave (+)-1,3-dimethyl-1-vinylindene. The homologous aldehyde (1; X = CH<sub>2</sub>CHO) was obtained by hydrolysis of the mixture of *cis*- and

<sup>1</sup> Part 13, D. W. Jones and G. Kneen, *J.C.S. Perkin I*, 1976, 1313.

<sup>2</sup> I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' Wiley, London, 1976; K. N. Houk, *Accounts Chem. Res.*, 1975, **8**, 361; K.-L. Mok and M. J. Nye, *J.C.S. Perkin I*, 1975, 1810.

<sup>3</sup> E.g., B. J. Arnold, P. G. Sammes, and T. W. Wallace, *J.C.S. Perkin I*, 1974, 409, 415; C. W. Jefford, A. F. Boschung, and C. G. Rimbault, *Tetrahedron Letters*, 1974, 3387; R. Huisgen and H. Mayr, *J.C.S. Chem. Comm.*, 1976, 55, 57; M. J. S. Dewar and L. E. Wade, *J. Amer. Chem. Soc.*, 1973, **95**, 290; G. R. Krow and J. Reilly, *ibid.*, 1975, **97**, 3837; D. A. Evans and A. M. Golob, *ibid.*, p. 4765.

<sup>4</sup> (a) P. Schiess and P. Funschilling, *Tetrahedron Letters*, 1972, 5195, and cited references; (b) D. J. Field, D. W. Jones, and G. Kneen, *J.C.S. Chem. Comm.*, 1975, 754, and cited references; (c) L. L. Miller and R. F. Boyer, *J. Amer. Chem. Soc.*, 1971, **93**, 650; (d) L. A. Paquette and M. J. Carmody, *ibid.*, 1975, **97**, 5841; T. L. Gilchrist, C. J. Moody, and C. W. Rees, *J.C.S. Chem. Comm.*, 1976, 414; (e) C. D. Anderson, J. T. Sharp, E. Stefaniuk, and R. S. Strathdee, *Tetrahedron Letters*, 1976, 305.

<sup>5</sup> (a) D. W. Jones and G. Kneen, *Chem. Comm.*, 1971, 1356; (b) D. J. Field, D. W. Jones, and G. Kneen, *J.C.S. Chem. Comm.*, 1976, 873; (c) M. F. Semmelhack, H. N. Weller, and J. S. Foas, *J. Amer. Chem. Soc.*, 1977, **99**, 293.

*trans*-olefins formed by reaction of (1; X = CHO) with methoxymethylenetriphenylphosphorane. Reaction of (+)-(1; X = CHO) with chloromethylenetriphenyl-

Optically active 1,3-dimethylindene was prepared by the method of Bergson and his collaborators.<sup>7</sup>

*Racemisation of the Indenes (1).*—When heated in

Rate data for racemisation of the indenes (1)

Indene (1) X =	Solvent	$10^5 k_{\text{rac}}/s^{-1}$ at stated temperature (°C)	$\Delta S^\ddagger/\text{cal K}^{-1} \text{ mol}^{-1}$	$\Delta H^\ddagger/\text{kcal mol}^{-1}$
(i)	Ph <sub>2</sub> O	2.42 ± 0.05 (50)	-11.41 ± 2.21	22.08 ± 0.75
		6.49 ± 0.06 (60)		
		20.40 ± 0.56 (70)		
		47.08 ± 0.47 (80)		
		5 480 (140) <sup>a</sup>		
(ii) CHO	Me <sub>2</sub> NCHO	6.62 ± 0.02 (60)	-6.20 ± 0.25	23.84 ± 0.08
		19.70 ± 0.10 (70)		
		32.94 ± 0.14 (75)		
		54.05 ± 0.12 (80)		
(iii) CHO	Me <sub>2</sub> SO	22.79 ± 0.20 (70)		
(iv) CHO	Decalin	15.15 ± 0.03 (70)		
(v) Ac	Ph <sub>2</sub> O	5.11 ± 0.11 (140)	-10.23 ± 1.16	28.31 ± 0.50
		11.46 ± 0.27 (150)		
		25.60 ± 0.47 (160)		
		39.20 ± 0.57 (165)		
		3.14 ± 0.05 (140)		
(vi) Ac	Me <sub>2</sub> NCHO	65.86 ± 1.26 (160)		
(vii) COPr <sup>t</sup>	Ph <sub>2</sub> O	5.56 ± 0.10 (255)		
(viii) CO <sub>2</sub> Me	Ph <sub>2</sub> O	3.82 ± 0.24 (255) <sup>b</sup>		
		1.65 ± 0.01 (225)		
(ix) CO <sub>2</sub> Ph	Ph <sub>2</sub> O	5.51 ± 0.08 (240)	-7.51 ± 0.49	36.77 ± 0.25
		10.27 ± 0.06 (250)		
		14.46 ± 0.08 (255)		
		0.000 65 (140) <sup>a</sup>		
		15.9 ± 0.06 (255) <sup>b</sup>		
(x) CO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> - <i>p</i>	Ph <sub>2</sub> O	23.3 (255) <sup>b</sup>		
(xi) CONHMe	Ph <sub>2</sub> O	4.30 ± 0.21 (245)		
(xii) H	Ph <sub>2</sub> O	ca. 0.05 (140) <sup>c,d</sup>		
(xiii) C≡CH	Ph <sub>2</sub> O	ca. 0.22 (245) <sup>d</sup>		
(xiv) C≡N	Ph <sub>2</sub> O	ca. 0.19 (245) <sup>d</sup>		
(xv) CH=CH <sub>2</sub>	Ph <sub>2</sub> O	1.79 ± 0.04 (210)	-11.09 ± 3.28	33.85 ± 1.64
		3.37 ± 0.07 (220)		
		7.89 ± 0.20 (230)		
		14.29 ± 0.11 (240)		
		0.003 75 (140) <sup>a</sup>		
(xvi) Bz	Ph <sub>2</sub> O	4.97 ± 0.02 (140)	-8.76 ± 0.88	28.91 ± 0.37
		12.11 ± 0.06 (150)		
		27.44 ± 0.15 (160)		
		58.07 ± 0.35 (170)		
		146 (180) <sup>a</sup>		
(xvii) COC <sub>6</sub> H <sub>4</sub> SO <sub>2</sub> Me- <i>p</i>	Ph <sub>2</sub> O	4.09 ± 0.03 (130)	-7.20 ± 0.45	28.98 ± 0.19
		10.23 ± 0.04 (140)		
		23.58 ± 0.16 (150)		
		54.55 ± 0.14 (160)		
(xviii) COC <sub>6</sub> H <sub>4</sub> OMe- <i>p</i>	Ph <sub>2</sub> O	75.7 ± 0.16 (180)		

<sup>a</sup> Value by extrapolation using the given activation parameters. <sup>b</sup> Rate of formation of the 2-isomer (2) (measured by n.m.r.).

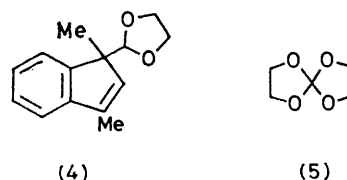
<sup>c</sup> Estimated rate prior to onset of catalysis; racemisation of 1-methyl-3-*t*-butylindene proceeds at a similar rate (J. Almy and D. J. Cram, *J. Amer. Chem. Soc.*, 1970, **92**, 4316); for deuterium shift in 1-deuterio-1,3-dimethylindene see P. E. Rakita and G. A. Taylor, *Inorg. Chem.*, 1972, **22**, 2136. <sup>d</sup> Maximum racemisation rate constant; optical activity loss may be due to general thermal decomposition.

phosphorane and dehydrochlorination (NaNH<sub>2</sub>-NH<sub>3</sub>) of the mixture of olefins formed gave the acetylene (1; X = C≡CH). The nitrile (+)-(1; X = C≡N) was formed by conversion of (+)-(1; X = CHO) into its oxime followed by acetic anhydride dehydration. The (+)-aldehyde was converted at 20 °C into the (+)-ethylene acetal (4) using diethylene orthocarbonate (5).<sup>6,\*</sup> The esters (+)-(1; X = CO<sub>2</sub>Me) and (+)-1; X = CO<sub>2</sub>Ph) was prepared as previously described<sup>1</sup> for the racemic compounds. Reaction of (+)-(1; X = OAc) with methylamine gave the amide (1; X = CONHMe).

\* We thank Professor D. H. R. Barton for details of this work prior to its publication, and a generous sample of (5).

<sup>6</sup> D. H. R. Barton, C. C. Dawes, and P. D. Magnus, *J.C.S. Chem. Comm.*, 1975, 432.

diphenyl ether solution the indenes (1) generally underwent clean loss of optical activity; the losses of optical



activity provided good first-order plots. Rate constants and derived activation parameters are given in the Table. For the groups (X) migrating faster than

<sup>7</sup> A. M. Weidler and G. Bergson, *Acta Chem. Scand.*, 1964, **18**, 1483; L. Ohlsson, I. Wallmark, and G. Bergson, *ibid.*, 1966, **20**, 750.

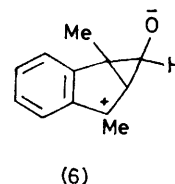
hydrogen in the isoindene intermediates (3) loss of optical activity involved simple racemisation; the ( $\pm$ )-indenenes (1) being formed. For the groups migrating more slowly than hydrogen loss of optical activity was accompanied by formation of the 2-acylindenenes (2). That optical activity loss involves *only* migration of the group X to C-2 of the indene system is supported by the near equality of the rate of optical activity loss, and the rate of formation of 2-acylindene when X = CO<sub>2</sub>Me [Table entry (viii)], or X = CO<sub>2</sub>Ph [entry (ix)]. At the other extreme very rapid formyl migration was shown<sup>4b</sup> only to involve migration of the formyl group to C-2 of the indene system. Convincing evidence for a concerted migration of the formyl group to C-2 of the indene system has also been provided.<sup>4b</sup>

*Discussion of Migratory Aptitude Data.*—Our results for different migrating acyl groups (Table) reveal a wide spread of migratory aptitudes; the formyl group migrates *ca.* 10<sup>3</sup> times more rapidly than acetyl which migrates *ca.* 10<sup>4</sup> times more rapidly than the methoxycarbonyl group. The formyl, acetyl, and benzoyl groups migrate more readily than hydrogen [entry (xii) Table], but the methoxycarbonyl group migrates *ca.* 10<sup>2</sup> times more slowly than hydrogen. Under similar conditions alkyl groups fail to migrate; (4) was recovered with its optical activity unchanged after being heated in diphenyl ether at 240 °C (3.5 h). Similarly (1; X = CH<sub>2</sub>OAc) and (1; X = CH<sub>2</sub>CHO) resisted racemisation at 245 °C. The failure of these compounds to racemise suggests that inductive effects are not responsible for the more ready migration of unsaturated than saturated groups. The slow migration of the ethynyl and nitrile groups [entries (xiii) and (xiv) Table] suggests that increased s-character in the migrating bond is not the dominant factor determining migratory aptitude. Improved transition state (t.s.) bridging by the hydrogen s-orbital compared to the sp<sup>2</sup>-orbital of a phenyl group or the sp<sup>3</sup>-orbital of a methyl group was suggested to explain the order of migratory aptitude H > Ph > Me observed in certain indenenes.<sup>8</sup>

Bond dissociation energies estimated for various alkyl-acyl bonds from heats of formation data<sup>9,\*</sup> fail to account for the observed migratory aptitudes. Thus the benzoyl group would be expected to migrate more rapidly than the formyl group since the bond dissociation energy of the alkyl-Bz bond (68 ± 5 kcal mol<sup>-1</sup>) is considerably less than that of the alkyl-CHO bond (80 ± 2 kcal mol<sup>-1</sup>). The formyl group in fact migrates *ca.* 10<sup>3</sup> times more rapidly than the benzoyl group.

When steric and other effects are very similar, migratory aptitude parallels increased electron-accepting ability in the migrating group. This is observed for the benzoylindenenes [entries (xvi)—(xviii)] and the phenyl and *p*-nitrophenyl esters [entries (ix) and (x)]. The

observed substituent effects are small however (<4) and indicate little polarity change in going from the ground state to the rearrangement t.s. This is supported by the small solvent effect observed for the racemisation of (1; X = CHO), which is only 1.3 times more rapid in dimethylformamide than in decalin [entries (ii) and (iv) Table]. A similar small rate increase is observed for racemisation of (1; X = CHO) in dimethyl sulphoxide. Comparison of the activation parameters for racemisation of (1; X = CHO) in diphenyl ether and dimethylformamide [entries (i) and (ii)] indicates a *greater* enthalpy of activation in the more polar solvent. Racemisation of (1; X = Ac) is slightly slower in dimethylformamide than in diphenyl ether. Related small solvent-polarity and substituent effects have been observed for the *ortho*-Claisen rearrangement<sup>10</sup> and the Diels-Alder reaction.<sup>11</sup> For the addition of *para*-substituted 1-phenylbutadienes to maleic anhydride the rate increases only *ca.* 10 times when the *para*-substituent is changed from NO<sub>2</sub> to OMe.<sup>12</sup> For the Diels-Alder reaction interaction between one pair of frontier molecular orbitals (commonly HOMO-diene and LUMO-dienophile) is assumed to be dominant,<sup>2</sup> yet this interaction fails to lead to significant detectable polarity increase in going to the addition t.s.



In the 1,5-shift of unsaturated groups, 1,5-formyl migration is *ca.* 10<sup>6</sup> times faster than 1,5-vinyl shift [entry (xv) Table]. This observation supports a correlation between the migratory aptitude of the group X and its electron-accepting ability. Since the inductive effect of two oxygen atoms fails to promote rearrangement in (4), the resonance electron-accepting ability of the migrating group appears to be determining. This involvement of the migrating  $\pi$ -system could be pictured either as a contribution to the t.s. from the resonance form (6), or as overlap between the indene HOMO ( $\pi_4$ ) and carbonyl LUMO ( $\pi^*$ ). Several ways in which such overlap could occur are shown for the simpler cyclopentadiene system in (7a), (7b), (8a), and (8b); benzo-substitution at C(4)-C(5) in these structures would generate the related indene system without materially changing the arguments presented below. In (7a) and (7b) the formyl group occupies a plane roughly perpendicular to that of the C(1)-C(2) bond whilst in (8a) and (8b) the plane of the formyl group bisects the C(5)-C(1)-C(2) angle. The formyl group can be arranged with its oxygen directed away from the cyclopentadiene

\* We thank Dr. M. E. Anthony for discussion.

<sup>8</sup> L. L. Miller, R. Greisinger, and R. F. Boyer, *J. Amer. Chem. Soc.*, 1969, **91**, 1578.

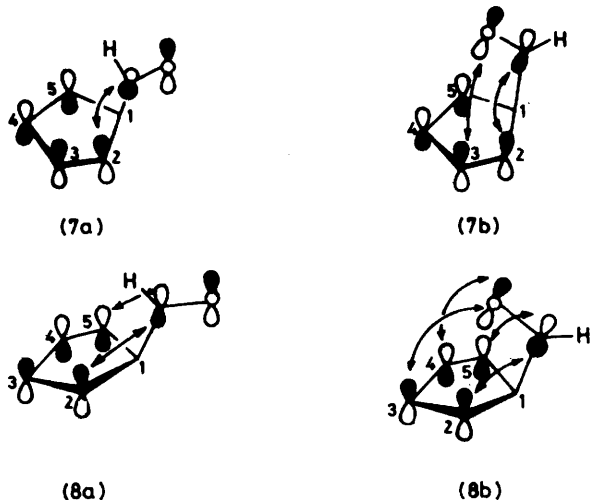
<sup>9</sup> J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, 1970.

<sup>10</sup> S. J. Rhoads, in 'Molecular Rearrangements,' Part 1, ed. P. de Mayo, Wiley, New York, 1963, p. 655.

<sup>11</sup> J. Sauer, *Angew. Chem. Internat. Edn.*, 1967, **6**, 16.

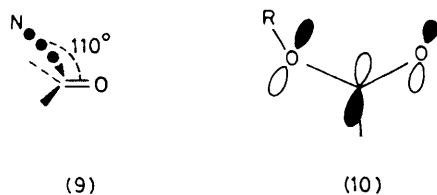
<sup>12</sup> P. V. Alston and R. M. Ottenbrite, *J. Org. Chem.*, 1974, **39**, 1584.

system as in (7a) and (8a) (*exo*-arrangement) or with the oxygen over the cyclopentadiene system as in (7b) and (8b) (*endo*-arrangement). The preferred trajectory of nucleophilic attack on a carbonyl group (9),<sup>13</sup> the spatial distribution of the carbonyl  $\pi^*$ -orbital,<sup>14</sup> and the presence of destabilising (secondary) interactions involving the oxygen  $\pi^*$ -exponent in the *endo*-arrangements



(7b) and (8b), all favour the *exo*-arrangements (7a) and (8a).

In view of the small substituent effects observed when steric and other effects are similar, the rapid decrease in migratory aptitude in the series  $\text{CHO} \geq \text{Ac} \geq \text{CO}_2\text{Me}$  although in accord with increasing energy of the carbonyl  $\pi^*$  orbital<sup>15</sup> is probably accentuated by other factors. The formyl group appears to be ideally constituted for migration *via* a preferred *exo*-arrangement; the carbon exponent of its low energy  $\pi^*$  orbital can be brought into good overlap with the carbon exponent at the cyclopentadiene C-2 (7a) or C-2 and C-5 (8a). For other acyl groups (RCO) a steric or electronic effect between the group R and the cyclopentadiene ring will tend to prevent such effective interaction. For acetyl migration



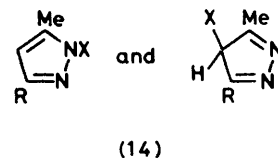
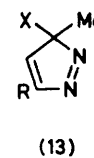
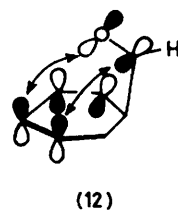
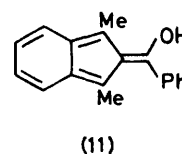
*via* the *exo*-arrangement (7a; Me replacing formyl-H) the methyl group will be brought into proximity with C-3 of the cyclopentadiene system so opposing the overlap of the orbital at C-2 with the carbonyl carbon atom. For methoxycarbonyl and related groups, *e.g.* CONHMe the  $\pi^*$ -orbital has the form shown in (10). Thus anti-bonding between the cyclopentadiene  $\pi$ -system and a

<sup>13</sup> H. B. Burgi, J. D. Dunitz, J. M. Lehn, and G. Wipff, *Tetrahedron*, 1974, **30**, 1563; J. E. Baldwin, *J.C.S. Chem. Comm.*, 1976, 734, 738.

$\pi^*$  coefficient at oxygen is unavoidable; for an arrangement of type (7b) this involves mainly the carbon exponent at C-3 whilst for an arrangement of type (8b) anti-bonding involves the carbon exponent at both C-3 and C-4.

Destabilising steric or secondary interaction effects will be enhanced if, as seems likely, orbital interactions are improved by reduction in the angle between the cyclopentadiene ring and the migrating  $\sigma$ -bond.

The observed (n.m.r.) rate of conversion of the 1-acylindenes (1) into the 2-acylindenes (2) ( $k_{\text{obs}}$ ) is related to the rate constant for the individual steps of the Scheme by the expression  $k_{\text{obs}} = k_1 k_2 / (k_{-1} + k_2)$  which can be rearranged to  $k_{-1}/k_2 = (k_1/k_{\text{obs}}) - 1$ . The ratio  $k_{-1}/k_2$  for a given acyl group is the relative migratory aptitude of that acyl group compared to hydrogen in the isoindene intermediate (3). Using previously measured values of



$k_{\text{obs}}$  and  $k_1$  values from the racemisation data (Table)  $k_{-1}/k_2$  is found to be  $2.3 \times 10^4$  (at 140 °C) for formyl migration, and 60 (at 200 °C) for acetyl migration. From the racemisation data (Table) formyl migration is  $10^5$  times and acetyl migration  $10^2$  times faster than the hydrogen shift. Although relative  $k_{\text{rac}}$  values and  $k_{-1}/k_2$  ratios provide similar relative migratory tendencies for formyl and acetyl groups compared to hydrogen exact correspondence would not be expected for the migrating groups are originating and become finally located in different environments. Use of  $k_{-1}/k_2$  ratios to determine migratory tendency assumes also that conversion of (3) into (2) involves only 1,5-sigmatropic hydrogen shift. For benzoyl migration the enol (11) or related enolate was suggested<sup>1</sup> as a likely intermediate in a suspected alternative route from the 2*H*-indene (3; X = Bz) to (2; X = Bz); in accord with such a mechanism the apparent  $k_{-1}/k_2$  ratio for Bz

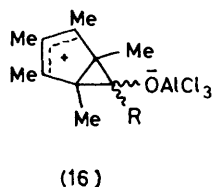
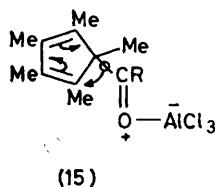
<sup>14</sup> W. L. Jorgensen and L. Salem, 'The Organic Chemist's Book of Orbitals,' Academic Press, New York, 1973.

<sup>15</sup> O. Eisenstein, J. M. LeFour, and C. Minot, *Tetrahedron Letters*, 1976, 1681.

migration (*ca.* 3.6) differs considerably from the relative migratory aptitudes of these groups (*ca.*  $10^3$ ) [Table entries (xii) and (xvi)]. As mentioned earlier the near equality of  $k_{rac.}$  and  $k_{obs.}$  for  $\text{CO}_2\text{Ph}$  migration shows that hydrogen shift is faster than  $\text{CO}_2\text{Ph}$  shift in the isoindene (3;  $\text{X} = \text{CO}_2\text{Ph}$ ). These observations show that the migratory aptitudes of acyl groups towards migration from C-2 to C-1 in the 2*H*-indenes (3) are in the order  $\text{HCO} > \text{MeCO} > \text{H} > \text{CO}_2\text{Ph}$  or  $\text{CO}_2\text{Me}$ , *i.e.* precisely the same order determined (Table) for migration from C-1 to C-2 in the indenes (1).

Similar migratory aptitude differences in cyclohexadienes ( $\text{HCO} > \text{Ac} > \text{H} > \text{CO}_2\text{Me}$ )<sup>16</sup> have been observed and can also be explained in terms of secondary interactions; the *endo*-arrangement (12) is again destabilised by secondary interaction involving the acyl oxygen atom. Acetyl migration is also more rapid than ester shift in the rearrangement of (13;  $\text{X} = \text{Ac}$  or  $\text{CO}_2\text{Me}$ ) to the isomers (14;  $\text{X} = \text{Ac}$  or  $\text{CO}_2\text{Me}$ ).<sup>17</sup> It appears, therefore, that the migratory aptitudes determined in this study for the indene system (Table) will be useful guides in assessing relative migratory aptitudes towards 1,5-shift over other diene and hetero-diene frameworks.

If interaction between the indene  $\psi_4$  orbital and the  $\pi^*$ -orbital of the carbonyl group is an important feature



of the 1,5-acyl shift the process should be accelerated by co-ordination of the carbonyl oxygen with acids or Lewis acids. Such co-ordination should lower the energy of the  $\pi^*$ -orbital and increase the carbon exponent of that orbital.<sup>18</sup> Indeed racemisation of (1;  $\text{X} = \text{Ac}$ ) is *ca.* 70 times faster in the presence of boron trifluoride-diethyl ether, and racemisation of (1;  $\text{X} = \text{Bz}$ ) is similarly accelerated. Certain acyl-pentamethylcyclopentadienes in the form of aluminium chloride complexes (15) undergo rapid degenerate shift of the complexed acyl group (15; arrows), and a bridged intermediate or t.s. (16) has been proposed.<sup>19</sup> For this rearrangement ester migration is also slow compared to acetyl migration. However the rearrangement (15; arrows) differs from the uncatalysed rearrangement of (1) in two respects. For the catalysed reaction benzoyl migration is *ca.* 700 times faster than acetyl migration [*cf.* Table entries (v) and (xvi)], and a *p*-methoxy-group retards the migration of a co-ordinated benzoyl group by *ca.*  $10^{-3}$  [*cf.* Table entries (xvi) and (xviii)]. We currently favour description of the interaction between

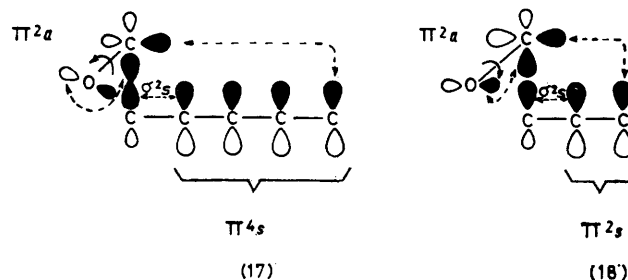
<sup>16</sup> P. Schiess and P. Funfschilling, *Tetrahedron Letters*, 1972, 5195.

<sup>17</sup> M. Franck-Neumann and C. D. Buchecker, *Tetrahedron Letters*, 1976, 2069.

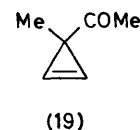
<sup>18</sup> *Cf.* N. T. Anh and J. Seyden-Penne, *Tetrahedron*, 1973, 29, 3259; K. N. Houk and R. W. Strozier, *J. Amer. Chem. Soc.*, 1973, 95, 4094.

the  $\pi$ -systems of the migrating group and diene unit as a *secondary interaction* which supports the *primary interactions* between the migrating  $\sigma$ -bond and the diene system. However, we cannot exclude full involvement of the  $\pi$ -system of the migrating group as an 'extra' component in the pericyclic process.

The 1,5-migration of a carbonyl or olefin system could be viewed as a  $\pi^4s + \sigma^2s + \pi^2a$  process as shown in (17).



Here antarafacial use of the migrating  $\pi$ -bond is secured by the anti-clockwise rotation shown. We do not favour this description since contrary to observation<sup>1,4b</sup> the 1,3-acyl shift would then be expected to be an easy, allowed  $\pi^2s + \sigma^2s + \pi^2s$  process (18) in which suprafacial involvement of the migrating  $\pi$ -system is secured by the clockwise rotation shown. However only for cyclopropenes is the 1,3-shift also a 1,2-migration and, therefore, subject to the same favourable geometrical factors prevailing for 1,5-shift in the cyclopentadiene system. Interestingly, (19) undergoes 1,3-acetyl migration at 140 °C.<sup>20</sup> The manner in which the migrating  $\pi$ -system is used in (17) and (18) is reminiscent of the  $\pi^2a +$



$\pi^2a + \sigma^2a$  description of the di- $\pi$ -methane rearrangement. In that rearrangement also the double bond essential for occurrence of rearrangement appears unchanged in the product.<sup>21</sup>

#### 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. Optical rotations were obtained using a Perkin-Elmer 141 or Thorn type 243 polarimeter. Petroleum refers to light petroleum (b.p. 60–80 °C) and chromatography<sup>22</sup> on silica

<sup>19</sup> R. F. Childs and M. Zeya, *J. Amer. Chem. Soc.*, 1974, 96, 6418.

<sup>20</sup> H. Monti and M. Bertrand, *Tetrahedron Letters*, 1970, 2591.

<sup>21</sup> H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *J. Amer. Chem. Soc.*, 1974, 96, 4630.

<sup>22</sup> B. J. Hunt and W. Rigby, *Chem. and Ind.*, 1967, 1868.

to short-column chromatography over Kieselgel G (Merck).

**Kinetic Measurements.**—Approximately 30 mg of the optically active indene was dissolved in the required solvent (usually diphenyl ether) (2 ml) in a 10 ml stoppered Pyrex test-tube drawn out at the centre. The optical rotation of the solution was measured; the solution was pipetted into the polarimeter cell, and when all air-bubbles had been removed, the rotation was measured at a constant temperature of 37 °C (this temperature prevented solidification of diphenyl ether solvent). The solution was recovered from the polarimeter cell and replaced in the Pyrex test-tube. The stoppered tube was then immersed in a Grant constant-temperature bath (containing water for measurements below 100 °C and Shell Nonidet P40 for measurements above 100 °C) previously stabilised at the required temperature ( $\pm 0.35$  °C). At regular intervals of time the tube was removed from the bath and immersed in a cold-water bath to quench rearrangement; the optical rotation of the solution was then measured. All racemisations were followed to at least 50% completion, and in most cases considerably more. In most cases straight lines were obtained from rate plots. All slopes, intercepts, and errors were obtained from a least-mean-squares programme fed into a Seiko S-301 calculator.

**Resolution of 1,3-Dimethylindene-1-carboxylic Acid.**—1,3-Dimethylindene-1-carboxylic acid (45 g) and quinine (78 g) were dissolved in ethanol and the volume reduced at 40 °C under reduced pressure. When set aside at 20 °C the salt of the (+)-acid was deposited (52 g). After one recrystallisation from ethanol this gave the pure diastereoisomer (37.3 g),  $[\alpha]_D - 32^\circ$  (*c* 1.97, CHCl<sub>3</sub>), which when shaken with sulphuric acid (1M) and ether gave (+)-1,3-dimethylindene-1-carboxylic acid (13.3 g),  $[\alpha]_D + 76^\circ$  (*c* 1.15, CHCl<sub>3</sub>), m.p. 93–96 °C (from petroleum).

Concentration of the mother liquor left after removal of the salt of the (+)-acid gave as a second crop the slowly crystallising and more soluble salt of the (–)-acid [38.79 g;  $[\alpha]_D - 154.6^\circ$  (*c* 0.65, CHCl<sub>3</sub>)]. After two recrystallisations from ethanol this gave 12.98 g of the salt of the (–)-acid,  $[\alpha]_D - 180^\circ$  (*c* 0.56, CHCl<sub>3</sub>). With dilute sulphuric acid this gave the (–)-acid (4.58 g),  $[\alpha]_D - 68.6^\circ$  (*c* 2.2, CHCl<sub>3</sub>).

A third crop (17.4 g) was obtained by addition of acetone to the original mother liquor. After two recrystallisations from ethanol this had  $[\alpha]_D - 142^\circ$  (*c* 0.49, CHCl<sub>3</sub>) (8.47 g), and was combined with material (8.3 g) from the mother liquors from recrystallisation of the second crop,  $[\alpha]_D - 137^\circ$  (*c* 1.605, CHCl<sub>3</sub>). Recrystallisation from ethanol failed to change significantly the rotation (12.08 g),  $[\alpha]_D - 137.85^\circ$  (*c* 0.745, CHCl<sub>3</sub>), and treatment with sulphuric acid gave acid,  $[\alpha]_D - 27.35^\circ$  (*c* 1.55, CHCl<sub>3</sub>).

**Preparation of Optically Active Indenes (I) previously prepared in Racemic Form.**—The (+)-acid (1; X = CO<sub>2</sub>H) was converted into the ester (1; X = CO<sub>2</sub>Me),  $[\alpha]_D + 75.3^\circ$  (*c* 2.32, CHCl<sub>3</sub>), the ester (1; X = CO<sub>2</sub>Ph),  $[\alpha]_D + 128.5^\circ$  (*c* 0.59, CHCl<sub>3</sub>), and the aldehyde (1; X = CHO),  $[\alpha]_D + 135^\circ$  (*c* 1.6, CHCl<sub>3</sub>), as previously described<sup>1</sup> for preparation of the corresponding racemic compounds. The (+)-aldehyde (1; X = CHO) was converted into the acetyl compound (1; X = Ac),  $[\alpha]_D + 126.5^\circ$  (*c* 0.957, CHCl<sub>3</sub>), and the benzoyl compound (1; X = Bz),  $[\alpha]_D + 242.76^\circ$  (*c* 0.975, CHCl<sub>3</sub>) as previously described<sup>1</sup> for the racemic compounds. The optically active products had n.m.r. spectra identical with those obtained earlier<sup>1</sup> for the (±)-compounds.

(+)-N,1,3-Trimethylindene-1-carboxamide.—(+)-Methyl

1,3-dimethylindene-1-carboxylate (231 mg, 1.14 mmol) and methylamine (10 ml) were allowed to react in a sealed tube at 20 °C (4 weeks). Evaporation of methylamine and crystallisation from benzene–light petroleum gave (+)-N,1,3-trimethylindene-1-carboxamide (1; X = CONHMe), m.p. 99–102 °C (Found: C, 77.7; H, 7.5; N, 7.2. C<sub>13</sub>H<sub>15</sub>NO requires C, 77.6; H, 7.5; N, 7.0%),  $\nu_{\max}$  (Nujol) 3 320, 3 290, and 1 640 cm<sup>-1</sup>;  $\tau$  (60 MHz) 2.25–2.75 (4 H, m, Ar), 3.78 (1 H, q, *J* 1.5 Hz), 4.59br (1 H, s, NH), 7.33 (3 H, d, *J* 4.5 Hz), 7.81 (3 H, d, *J* 1.5 Hz), 8.4 (3 H, s); *m/e* 201, 144, 129, and 128 (23, 100, 100, and 65%),  $[\alpha]_D + 68.0^\circ$  (*c* 1.043, CHCl<sub>3</sub>). The racemic compound prepared in the same way had m.p. 106–108 °C (from benzene–light petroleum).

N,1,3-Trimethylindene-2-carboxamide.—N,1,3-Trimethylindene-1-carboxamide (48 mg) and diphenyl ether (0.5 ml) were heated at 250 °C (27.5 h), and the product was chromatographed on silica; elution with methanol–chloroform (1 : 49) gave N,1,3-trimethylindene-2-carboxamide (25 mg, 52%), m.p. 158–161 °C (from benzene–light petroleum) (Found: C, 77.55; H, 7.35; N, 6.75. C<sub>13</sub>H<sub>15</sub>NO requires C, 77.6; H, 7.5; N, 6.95%),  $\nu_{\max}$  (Nujol) 3 290 and 1 620 cm<sup>-1</sup>,  $\lambda_{\max}$  (EtOH) 234sh and 279 nm ( $\epsilon$  10 850 and 13 620);  $\tau$  (60 MHz) 2.3–2.8 (4 H, m), 4.13br (1 H, s, NH), 6.31 (1 H, m), 7.01 (3 H, d, *J* 5 Hz), 7.60 (3 H, d, *J* 2 Hz), 8.65 (3 H, d, *J* 7.5 Hz); *m/e* 201, 171, 144, 129, and 128 (18, 15, 100, 66, and 34%).

**The Oxime of (+)-1,3-Dimethylindene-1-carbaldehyde.**—The aldehyde (95 mg, 0.55 mmol), in the minimum quantity of chloroform, was added to hydroxylamine hydrochloride (210 mg, 3.0 mmol) in aqueous ethanol. Pyridine (237 mg, 3.0 mmol) was added to the mixture which was stirred at 20 °C (1.5 h). The product was poured into ether and the organic layer washed with dilute hydrochloric acid and water, and then dried (MgSO<sub>4</sub>) and evaporated. The crude product (105 mg) was chromatographed on silica in ether–benzene (1 : 9) to give the oxime (1; X = CH=NOH) (94 mg, 91%) as a colourless oil (Found: *M*<sup>+</sup>, 187.0995. C<sub>12</sub>H<sub>13</sub>NO requires *M*, 187.0997),  $\nu_{\max}$  2 660–3 660, 1 635, and 1 615 cm<sup>-1</sup>;  $\tau$  (60 MHz) 1.12br (1 H, s, OH), 2.72 (4 H, m), 2.84 (1 H, s), 4.01 (1 H, q, *J* 1.5 Hz), 7.89 (3 H, d, *J* 1.5 Hz), 8.56 (3 H, s); *m/e* 187, 160, 154, 141, 129, and 128 (46, 35, 53, 82, 92, and 100%),  $[\alpha]_D + 83.1^\circ$  (*c* 1.16, CHCl<sub>3</sub>).

**Thermolysis of (+)-1,3-Dimethylindene-1-carbaldehyde Oxime.**—The oxime (62 mg) and diphenyl ether (2 ml) were heated at 140 °C (3.2 h). Chromatography of the product on silica in ether–benzene (1 : 19) gave the oxime of (+)-1,3-dimethylindene-1-carbaldehyde (24 mg, 39%), pure by n.m.r.,  $[\alpha]_D + 82.0^\circ$  (*c* 1.195, CHCl<sub>3</sub>).

(+)-1,3-Dimethylindene-1-carbonitrile.—(+)-1,3-Dimethylindene-1-carbaldehyde oxime (50 mg, 0.267 mmol) and acetic anhydride (3 ml) were heated under reflux (45 min). Evaporation of solvent under reduced pressure on a steam-bath gave the crude product (43 mg) which was chromatographed on silica (30 g); elution with benzene gave (+)-1,3-dimethylindene-1-carbonitrile (32.5 mg, 72%) as a colourless oil (Found: *M*<sup>+</sup>, 169.0892. C<sub>12</sub>H<sub>11</sub>N requires *M*, 169.0891),  $\nu_{\max}$  2 235, 1 622, and 1 383 cm<sup>-1</sup>;  $\tau$  (60 MHz) 2.62 (4 H, m), 3.93 (1 H, q, *J* 1.5 Hz), 7.87 (3 H, d, *J* 1.5 Hz), 8.36 (3 H, s); *m/e* 169, 154, 141, and 127 (69, 100, 22, and 36%),  $[\alpha]_D + 122.5^\circ$  (*c* 1.564, CHCl<sub>3</sub>).

(+)-1-Isobutyryl-1,3-dimethylindene.—(+)-1,3-Dimethylindene-1-carbaldehyde (100 mg, 0.58 mmol) in ether (3 ml) was added to isopropylmagnesium bromide [from

magnesium (200 mg) and isopropyl bromide (1.01 g) in ether (10 ml)] at 20 °C and the mixture was stirred (1 h). Saturated ammonium chloride solution was added to it and the ether layer was separated and washed with water; it was then dried (MgSO<sub>4</sub>), and evaporated. The product (111 mg) was chromatographed on silica in ether–benzene (1 : 9) to give the alcohol [1; X = CH(OH)CMe<sub>2</sub>] as a mixture of diastereoisomers (41 mg, 33%). Continued elution gave 1-hydroxymethyl-1,3-dimethylindene (51 mg, 50%). Chromium trioxide (185 mg, 1.85 mmol) was stirred with pure dry pyridine (292 mg, 3.7 mmol) in pure dry methylene chloride (5 ml) in a nitrogen atmosphere (15 min). A diastereoisomeric mixture of the alcohols [1; X = CH(OH)CMe<sub>2</sub>] (40 mg, 0.185 mmol) in methylene chloride (1 ml) was added and the mixture was stirred (15 min). Ether was added and the ether-soluble portion was washed with dilute sodium hydroxide solution, dilute hydrochloric acid, sodium hydrogen carbonate solution, and water, and then dried (MgSO<sub>4</sub>) and evaporated to give (+)-1-isobutyl-1,3-dimethylindene (1; X = COCHMe<sub>2</sub>) which crystallised from light petroleum at –78 °C, m.p. 65–67 °C (Found: *M*<sup>+</sup>, 214.1359. C<sub>15</sub>H<sub>18</sub>O requires *M*, 214.1358), *v*<sub>max</sub> (Nujol) 1 707 cm<sup>-1</sup>; *τ* (60 MHz) 2.68 (4 H, m, Ar), 3.95 (1 H, m, olefinic), 7.79 (3 H, d, *J* 1.5 Hz); 7.98 (1 H, m), 8.57 (3 H, s), 9.10 (3 H, d, *J* 7 Hz), 9.32 (3 H, d, *J* 7 Hz), *m/e* 214, 213, 171, and 143 (9, 43, 13, and 100%), [α]<sub>D</sub> + 104.5° (*c* 0.844, CHCl<sub>3</sub>). Attempted addition of *t*-butylmagnesium chloride to (1; X = CHO) gave only 1-hydroxymethyl-1,3-dimethylindene.

(+)-1-*p*-Methoxybenzoyl-1,3-dimethylindene.—(+)-1,3-Dimethylindene-1-carbaldehyde (86 mg, 0.5 mmol) in ether (*ca.* 1 ml) was added to *p*-methoxyphenylmagnesium bromide [from *p*-bromoanisole (935 mg) and magnesium (130 mg) in refluxing ether (*ca.* 10 ml) over 2 h] at 20 °C and the mixture was stirred (2 h). The product was treated with ammonium chloride solution, and the ether layer washed with water, dried (MgSO<sub>4</sub>), and evaporated. Chromatography on silica in ether–benzene (1 : 19) gave a diastereoisomeric mixture of the alcohols [1; X = CH(OH)C<sub>6</sub>H<sub>4</sub>OMe-*p*] (115 mg, 82%) (Found: *M*<sup>+</sup>, 280.1463. C<sub>19</sub>H<sub>20</sub>O<sub>2</sub> requires *M*, 280.1458), *v*<sub>max</sub> 3 460 cm<sup>-1</sup>; *τ* 2.5–3.4 (8 H, m), 4.0 and 4.08 (total 1 H, both q, *J* 1.5 Hz, olefinic H of two diastereoisomers), 5.19br and 5.43br (1 H, both s), 6.27 (3 H, s), 7.82br (1 H, s, OH), 7.97 (3 H, d, *J* 1.5 Hz), 8.68 and 8.79 (3 H, both s).

The foregoing mixture (110 mg, 0.393 mmol) was oxidised with chromium trioxide (300 mg, 3 mmol) and pyridine (474 mg, 6 mmol) as described in the preceding experiment. After the usual work-up chromatography on silica in ether–benzene (1 : 19) gave (+)-1-*p*-methoxybenzoyl-1,3-dimethylindene (1; X = COC<sub>6</sub>H<sub>4</sub>OMe-*p*) (90 mg, 82.5%), m.p. 59–61 °C (from petroleum at 0 °C) (Found: C, 82.0; H, 6.4. C<sub>19</sub>H<sub>18</sub>O<sub>2</sub> requires C, 82.0; H, 6.5%), *v*<sub>max</sub> (Nujol) 1 660 cm<sup>-1</sup>; *τ* 2.5–2.9 (6 H, m, Ar), 3.38 (2 H, m, Ar), 3.73 (1 H, q, *J* 1.5 Hz), 6.29 (3 H, s), 7.80 (3 H, d, *J* 1.5 Hz), and 8.45 (3 H, s); [α]<sub>D</sub> 262.5° (CHCl<sub>3</sub>).

(+)-1-*p*-Methylthiobenzoyl-1,3-dimethylindene.—(+)-1,3-Dimethylindene-1-carbaldehyde (86 mg, 0.5 mmol) in ether (*ca.* 1 ml) was added dropwise to *p*-methylthiophenylmagnesium bromide [from *p*-bromothioanisole (1.02 g) and magnesium turnings (130 mg) (activated by washing with dilute hydrochloric acid, washing with water, washing with ethanol and ether, and oven drying) in ether under reflux in a nitrogen atmosphere (18 h)] and the mixture was stirred at 20 °C (2 h). The product was poured into

ammonium chloride solution and extracted with ether. The combined extracts were washed with water, dried (MgSO<sub>4</sub>), and evaporated to give the diastereoisomeric alcohols [1; X = CH(OH)C<sub>6</sub>H<sub>4</sub>SMe] (130 mg, 88%) (Found: *M*<sup>+</sup>, 296.1235. C<sub>19</sub>H<sub>20</sub>OS requires *M*, 296.1228), *v*<sub>max</sub> 3 440 cm<sup>-1</sup>; *τ* 2.5–3.0 (8 H, m), 4.06 and 4.15 (1 H, both q, *J* 1.5 Hz, olefinic protons in the diastereoisomeric alcohols), 5.30 and 5.55br (1 H, both s), 7.63 (3 H, s), 7.73br (1 H, s, OH), 7.98br (3 H, s), 8.72 and 8.80 (3 H, both s).

The foregoing mixture of diastereoisomeric alcohols was oxidised with chromium trioxide (262 mg) and pyridine (428 mg) in methylene chloride (10 ml) as previously described. Work-up as described above and chromatography on silica in benzene–ether (19 : 1) gave (+)-1-*p*-methylthiobenzoyl-1,3-dimethylindene (1; X = COC<sub>6</sub>H<sub>4</sub>SMe) (80 mg, 62%) (Found: *M*<sup>+</sup>, 294.1078. C<sub>19</sub>H<sub>18</sub>SO requires *M*, 294.1070), *v*<sub>max</sub> 1 670 cm<sup>-1</sup>; *τ* 2.5–3.3 (8 H, m), 3.79 (1 H, q, *J* 1.5 Hz), 7.65 (3 H, s), 7.79 (3 H, d, *J* 1.5 Hz), and 8.49 (3 H, s).

(+)-1-*p*-Methylsulphonylbenzoyl-1,3-dimethylindene.—The foregoing sulphide (80 mg), periodic acid (3 ml, 1.4M); and methanol (1.5 ml) were heated at 60–70 °C (1.5 h). The mixture was cooled and extracted with ether and the ether extracts were washed with sodium thiosulphate solution and water, and then dried (MgSO<sub>4</sub>) and evaporated; the residue was chromatographed on silica in benzene–ether (9 : 1) to give (+)-1-*p*-methylsulphonylbenzoyl-1,3-dimethylindene (1; X = COC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Me-*p*) (35 mg, 40%), m.p. 139–140 °C (from ethanol) (Found: C, 70.15; H, 5.85. C<sub>19</sub>H<sub>18</sub>SO<sub>3</sub> requires C, 69.9; H, 5.5%), *v*<sub>max</sub> (Nujol) 1 676, 1 312, and 1 150 cm<sup>-1</sup>; *τ* 2.3 (2 H, d, *J* 9 Hz, Ar), 2.45–2.9 (6 H, m, Ar), 3.83 (1 H, q, *J* 1.5 Hz), 7.05 (3 H, s), 7.83 (3 H, d, *J* 1.5 Hz), and 8.42 (3 H, s); [α]<sub>D</sub> + 155.8° (CHCl<sub>3</sub>).

(+)-1,3-Dimethyl-1-vinylindene.—Butyl-lithium (205 mg, 3.2 mmol) in hexane (1.27 ml) was syringed into a slurry of methyltriphenylphosphonium bromide (1.25 g, 3.5 mmol) in ether (50 ml) at 0 °C under nitrogen. The yellow solution was stirred at 0 °C (2 h) and (+)-1,3-dimethylindene-1-carbaldehyde (500 mg, 2.9 mmol) in ether (8 ml) added. The white suspension was stirred (30 min) before addition of water. The ethereal layer was washed with water, dried (MgSO<sub>4</sub>), and evaporated, and the product chromatographed on alumina in benzene–petroleum (1 : 9) to give (+)-1,3-dimethyl-1-vinylindene (190 mg, 38%) as a colourless oil (Found: *M*<sup>+</sup>, 170.1095. C<sub>13</sub>H<sub>14</sub> requires *M*, 170.1095), *v*<sub>max</sub> (CHCl<sub>3</sub>) 1 630 cm<sup>-1</sup>; *τ* (60 MHz) 2.77 (4 H, s, Ar), 4.00 (1 H, q, *J* 1.5 Hz), 4.20 (1 H, dd, *J* 17 and 10 Hz), 4.90 (1 H, dd, *J* 17 and 2 Hz), 5.02 (1 H, dd, *J* 10 and 2 Hz), 7.90 (3 H, d, *J* 1.5 Hz), and 8.62 (3 H, s); *m/e* 170, 155, 153, 128, and 115 (100, 100, 52, 44, and 37%); [α]<sub>D</sub> + 51.6° (*c* 0.68, CHCl<sub>3</sub>).

*cis*- and *trans*-(+)-1-Chlorovinyl-1,3-dimethylindenes.—Butyl-lithium (595 mg, 9.3 mmol) in hexane (7.3 ml) was syringed into a slurry of chloromethylenetriphenylphosphonium chloride (3.27 g, 9.4 mmol) and piperidine (825 mg, 9.7 mmol) in ether (60 ml) at 20 °C in a nitrogen atmosphere. The yellow solution was stirred (1 h) and then (+)-1,3-dimethylindene-1-carbaldehyde (400 mg, 2.32 mmol) in ether (5 ml) was added, and the mixture stirred (1 h) before addition of water. The ether layer was washed with water, dried (MgSO<sub>4</sub>), evaporated, and the crude product (1.83 g) was chromatographed on 20% silver nitrate on silica (60 g); elution with benzene–petroleum (1 : 19) gave (+)-1-*trans*-chlorovinyl-1,3-dimethylindene (99 mg) as a colourless oil

(Found:  $M^+$ , 204.0703.  $C_{13}H_{13}^{35}Cl$  requires  $M$ , 204.0706),  $\nu_{\max}$  1 610  $cm^{-1}$ ;  $\tau$  (60 MHz) 2.75 (4 H, m, Ar), 3.93 (1 H, d,  $J$  13 Hz), 4.05 (1 H, q,  $J$  1.5 Hz), 4.06 (1 H, d,  $J$  13 Hz), 7.91 (3 H, d,  $J$  1.5 Hz), and 8.65 (3 H, s);  $m/e$  204, 189, 169, 153, 143, and 128 (84, 48, 100, 64, 39, and 35%);  $[\alpha]_D + 162.3^\circ$  ( $c$  1.345,  $CHCl_3$ ).

Continued elution gave first a mixture of the *cis*- and *trans*-olefins (218 mg) and then (+)-1-*cis*-chlorovinyl-1,3-dimethylindene (86 mg) as a colourless oil (Found:  $M^+$ , 204.0697.  $C_{13}H_{13}^{35}Cl$  requires  $M$ , 204.0706),  $\nu_{\max}$  1 620  $cm^{-1}$ ;  $\tau$  (90 MHz) 2.5—3.0 (4 H, m), 3.62 (1 H, q,  $J$  1.5 Hz), 4.06 (1 H, d,  $J$  8 Hz), 4.09 (1 H, d,  $J$  8 Hz), 7.89 (3 H, d,  $J$  1.5 Hz), 8.48 (3 H, s);  $m/e$  204, 189, 169, 153, 141, and 128 (89, 48, 100, 58, 30, and 28%);  $[\alpha]_D + 207.5^\circ$  ( $c$  0.925,  $CHCl_3$ ). Total yield 403 mg (85%).

(+)-1-Ethynyl-1,3-dimethylindene.—Sodium (101 mg) and a few crystals of hydrated ferric nitrate were added to liquid ammonia (100 ml) at  $-78^\circ C$  and the mixture stirred at  $-78^\circ C$  (1 h) before addition of a mixture of *cis*- and *trans*-(+)-1-chlorovinyl-1,3-dimethylindene (100 mg, 0.49 mmol) in dry ether (5 ml). After being stirred at  $-78^\circ C$  (3 h) the mixture was evaporated under nitrogen overnight. Ammonium chloride solution and ether were added to the residue and the ether layer was washed with water, dried ( $MgSO_4$ ), and evaporated. Chromatography of the product (77 mg) on silica in benzene-petroleum (1 : 19) gave starting material (25 mg) followed by (+)-1-ethynyl-1,3-dimethylindene (30 mg, 49%) as a colourless oil (Found:  $M^+$ , 168.0936.  $C_{13}H_{12}$  requires  $M$ , 168.0939),  $\nu_{\max}$  3 290, 2 110, and 1 620  $cm^{-1}$ ;  $\tau$  (60 MHz) 2.4—2.9 (4 H, m), 3.94 (1 H, q,  $J$  1.5 Hz), 7.91 (1 H, s), 7.91 (3 H, d,  $J$  1.5 Hz), and 8.46 (3 H, s);  $m/e$  168, 153, 141, 128, and 115 (21, 26, 17, 14, and 99%);  $[\alpha]_D + 150.0^\circ$  ( $c$  1.10,  $CHCl_3$ ).

*cis*- and *trans*-(+)-1-Methoxyvinyl-1,3-dimethylindene.—Phenyl-lithium (294 mg, 3.5 mmol) in ether (4.6 ml) was syringed into a slurry of methoxymethylenetriphenylphosphonium chloride (1.2 g, 3.5 mmol) in ether (20 ml) at  $20^\circ C$  under a nitrogen atmosphere. After 15 min the deep red solution was cooled to  $-30^\circ C$  and (+)-1,3-dimethylindene-1-carbaldehyde (200 mg, 1.16 mmol) in ether (2 ml) was added to it. After the mixture had been stirred at  $-30^\circ C$  (30 min) and  $20^\circ C$  (90 min), water was added to it; the ether layer was washed with water, dried ( $MgSO_4$ ), and evaporated. The crude product (458 mg) was chromatographed on silica; elution with benzene-petroleum (3 : 7) gave the impure (+)-*cis* form of the title compound (111 mg) as a colourless oil,  $\nu_{\max}$  1 657  $cm^{-1}$ ;  $\tau$  (90 MHz) 2.5—3.0 (4 H, m, Ar, and 6 H, impurity), 3.64 (1 H, q,  $J$  1.5 Hz), 4.19 (1 H, d,  $J$  6 Hz), 5.54 (1 H, d,  $J$  6 Hz), 6.50 (3 H, s), 7.92 (3 H, d,  $J$  1.5 Hz), and 8.52 (3 H, s). This product could not be further purified by distillation, chromatography, or crystallisation. Continued elution of the column gave the (+)-*trans*-compound (20 mg) as a colourless oil (Found:  $M^+$ , 200.1198.  $C_{14}H_{16}O$  requires  $M$ , 200.1201),  $\nu_{\max}$  1 667, 1 650, and 1 622  $cm^{-1}$ ;  $\tau$  (90 MHz) 2.75 (4 H, m, Ar), 3.58 (1 H, d,  $J$  13 Hz), 4.01 (1 H, q,  $J$  1.5 Hz), 5.13 (1 H, d,  $J$  13 Hz), 6.53 (3 H, s), 7.89 (3 H, d,  $J$  1.5 Hz), and 8.64 (3 H, s);  $m/e$  200, 185, 153, 141, 128, and 115 (100, 85, 23, 39, 18, and 25%);  $[\alpha]_D + 103^\circ$  ( $c$  0.965,  $CHCl_3$ ).

(+)-1,3-Dimethyl-1-(2-oxoethyl)indene (1; X =  $CH_2CHO$ ).—A crude mixture of *cis*- and *trans*-(+)-1-methoxyvinyl-1,3-dimethylindene prepared as above from (+)-1,3-dimethylindene-1-carbaldehyde (135 mg, 0.785 mmol), was

dissolved in ether (2 ml) previously saturated with 72% perchloric acid; <sup>23</sup> the mixture was then set aside at  $20^\circ C$  (30 min). After addition of ether the product was washed with water, saturated sodium hydrogen carbonate solution, and water, and then dried ( $MgSO_4$ ) and evaporated. The crude product (257 mg) was chromatographed on silica (45 g) in petroleum-benzene (1 : 4) to give (+)-1; X =  $CH_2CHO$  (50 mg) as an oil (Found:  $M^+$ , 186.1039.  $C_{13}H_{14}O$  requires  $M$ , 186.1044),  $\nu_{\max}$  1 725 and 1 620  $cm^{-1}$ ;  $\tau$  (60 MHz) 0.87 (1 H, t,  $J$  3 Hz, CHO), 2.5—2.9 (4 H, m), 3.87 (1 H, q,  $J$  1.5 Hz), 7.31 (2 H, d,  $J$  3 Hz), 7.90 (3 H, d,  $J$  1.5 Hz), and 8.66 (3 H, s);  $m/e$  186, 157, 144, 128, and 115 (15, 21, 100, 56, and 27%);  $[\alpha]_D + 47.3^\circ$  ( $c$  0.538,  $CHCl_3$ ).

This aldehyde (35 mg) was heated at  $245^\circ C$  (1.75 h) in diphenyl ether (2 ml); the recovered aldehyde (27 mg) [silica chromatography in petroleum-benzene (1 : 4)] showed almost complete retention of optical activity,  $[\alpha]_D + 46.6^\circ$  ( $c$  1.355,  $CHCl_3$ ).

1-Acetoxyethyl-1,3-dimethylindene.—To pure ethyl acetate (50 ml) was added 0.05 ml of 72% perchloric acid; 10 ml of this solution was added to pure ethyl acetate (30 ml) and pure acetic anhydride (4.8 ml) and the solution was made up to 50 ml with ethyl acetate.<sup>24</sup> (+)-1-Hydroxymethyl-1,3-dimethylindene (100 mg, 0.575 mmol) was dissolved in the above reagent (10 ml) and the mixture was set aside at  $20^\circ C$  (5 min). The product was diluted with ether and the organic layer washed with saturated sodium hydrogen carbonate solution, dried ( $MgSO_4$ ), and evaporated. A few ml of methanol containing a trace of pyridine was added and the solution was again evaporated. The product was chromatographed on silica in ether-benzene (1 : 9) to give (+)-1-acetoxyethyl-1,3-dimethylindene (60 mg, 48%) as a colourless oil (Found:  $M^+$ , 216.1149.  $C_{14}H_{16}O_2$  requires  $M$ , 216.1150),  $\nu_{\max}$  1 740  $cm^{-1}$ ;  $\tau$  (60 MHz) 2.70 (4 H, m, Ar), 3.95 (1 H, q,  $J$  1.5 Hz), 5.87 (1 H, d,  $J$  11 Hz), 5.99 (1 H, d,  $J$  11 Hz), 7.90 (3 H, d,  $J$  1.5 Hz), 7.95 (3 H, s), and 8.67 (3 H, s);  $m/e$  216, 156, 143, 141, 128, and 115 (11, 69, 65, 39, 36, and 17%);  $[\alpha]_D + 32.6^\circ$  ( $c$  1.21,  $CHCl_3$ ). This product in diphenyl ether (2 ml) was heated at  $200^\circ C$  (1 h) and  $245^\circ C$  (1.5 h), and recovered by silica chromatography in benzene in 16.5 mg yield,  $[\alpha]_D + 32.0^\circ$  ( $c$  1.64,  $CHCl_3$ ).

(+)-1-(Dioxolan-2-yl)-1,3-dimethylindene.—To (+)-1,3-dimethylindene-1-carbaldehyde (23.3 mg, 0.135 mmol) in dry ethanol-free chloroform (2 ml) was added diethylene orthocarbonate<sup>6</sup> (60 mg, 0.485 mmol) and *p*-toluenesulphonic acid (3 mg). After being stirred at  $20^\circ C$  (2 h) the mixture was diluted with ether, washed with saturated sodium hydrogen carbonate solution and water, dried ( $MgSO_4$ ), and evaporated. The crude product (30 mg) was chromatographed on silica in benzene to give (+)-1-(dioxolan-2-yl)-1,3-dimethylindene (28 mg, 96%) as a colourless oil (Found:  $M^+$ , 216.1144.  $C_{14}H_{16}O_2$  requires  $M$ , 216.1150);  $\tau$  (60 MHz) 2.70 (4 H, m), 3.92 (1 H, q,  $J$  1.5 Hz), 5.42 (1 H, s), 6.09 (4 H, m), 7.88 (3 H, d,  $J$  1.5 Hz), and 8.69 (3 H, s);  $m/e$  216, 157, 143, 141, 128, 115, 73, and 45 (70, 14, 50, 63, 100, 46, 100, and 100%);  $[\alpha]_D + 50.2^\circ$  ( $c$  0.39,  $CHCl_3$ ),  $[\alpha]_D + 48.5^\circ$  ( $c$  1.11,  $Ph_2O$ ). The ethylene acetal (10 mg) in diphenyl ether (1 ml) was heated at  $200^\circ C$  (1 h) and  $240^\circ C$  (3.5 h). The recovered acetal (8.5 mg) (silica chromatography in benzene) was pure as judged by its n.m.r. spectrum and had lost little optical activity,  $[\alpha]_D + 47.5^\circ$  ( $c$  0.415,  $Ph_2O$ ).

Racemisation of (+)-1-Acetyl-1,3-dimethylindene in the

<sup>24</sup> B. E. Edwards and P. N. Rao, *J. Org. Chem.*, 1966, **31**, 324.

<sup>23</sup> S. G. Levine, *J. Amer. Chem. Soc.*, 1958, **80**, 6150.



*Presence of Boron Trifluoride-Diethyl Ether.*—(+)-1-Acetyl-1,3-dimethylindene (55 mg, 0.296 mmol),  $[\alpha]_D^{20} +126.5^\circ$  ( $c$  0.957,  $\text{CHCl}_3$ ), and pure boron trifluoride-diethyl ether (50 mg, 0.352 mmol) were boiled under reflux in benzene (3 ml) for 9 h 22 min. After dilution with ether and washing with water the organic layer was dried ( $\text{MgSO}_4$ ) and evaporated, and the crude product chromatographed on silica (40 g) in benzene to recover the acetyl compound in partially racemised form (50 mg),  $[\alpha]_D^{20} +97.0^\circ$  ( $c$  1.663,  $\text{CHCl}_3$ ).

*Racemisation of (+)-1-Benzoyl-1,3-dimethylindene in the Presence of Boron Trifluoride-Diethyl Ether.*—(+)-1-Benzoyl-1,3-dimethylindene (120 mg),  $[\alpha]_D^{30} 242.76^\circ$  ( $c$  0.975,  $\text{CHCl}_3$ ), boron trifluoride-diethyl ether (85 mg), and benzene (5 ml) were heated in a sealed tube ( $\text{N}_2$ -atmosphere) in a constant-temperature bath at  $80^\circ\text{C}$  (6 h). The recovered benzoyl compound (90 mg) [silica chromatography in benzene-petroleum (3:1)] was pure as judged by its n.m.r. spectrum and had  $[\alpha]_D^{20} 171.45^\circ$  ( $c$  1.1,  $\text{CHCl}_3$ ).

[7/1796 Received, 12th October, 1977]

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