o-Quinonoid Compounds. Part 13.[1] 1,5-Acyl Shifts in Substituted Indenes; Conversion of 1-Acyl- into 2-Acyl-indenes and Orienting Mechanistic Experiments

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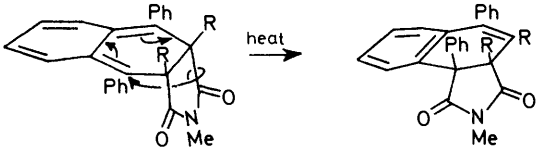
The 1-acyl-1,3-diphenylindenes (3; R = Ph) with acyl(X) = CHO, COMe, COPh, CONHMe, or CO_2Me have been prepared and shown to undergo thermal rearrangement to the corresponding 2-acylindenes (5; R = Ph). The 1-acyl-1,3-dimethylindenes (3; R = Me) with X = CHO, COMe, COPh, $CO_2{\cdot}C_6H_4{\cdot}NO_2(p)$, COPh, or CO_2Me were prepared similarly and shown to undergo slower thermal rearrangement to 2-acylindenes (5; R = Me). A mechanism for the rearrangement involving formation of the 2*H*-indenes (4) is supported by the results of trapping experiments with *N*-phenylmaleimide. These trapping experiments, together with evidence for basic catalysis of the rearragement for (3; R = Ph, X = CHO or COMe) and experiments on transfer of non-equilibrium spin with (3; R = Me, X = CHO), reveal the occurrence of rapid degenerate formyl and acetyl migration in these indenes. More rapid migration of acetyl than of hydrogen in the 2*H*-indene intermediate (9) is consistent with thermal conversion of 1-acetyl-3-methyl-1-phenylindene (8) into the 1-methyl-3-phenyl isomer (10). In contrast to formyl, acetyl, and benzoyl groups, ester groups (CO_2R) migrate more slowly than hydrogen in the 2*H*-indene intermediates (4); accordingly the rates of rearrangement of 1- to 2-substituted esters provide migratory aptitude data for these groups. Migratory aptitude increases in the order $CO_2Me < CO_2Ph < CO_2{\cdot}C_6H_4NO_2(p)$ for the indenes (3; R = Me). Preliminary tests support a concerted mechanism for the 1,5-shift of the acyl groups.

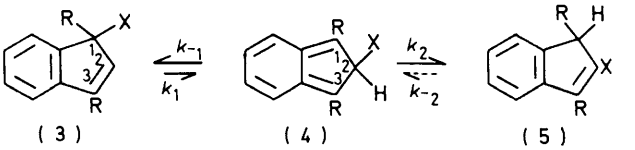
We have shown [2] that certain sterically stabilised *o*-quinodimethanes undergo ready 1,5-shift of an imido-group, and that migration of the acyl group occurs in preference to alkyl migration, *e.g.* (1) ⟶ (2) (Scheme 1).



R = Me or RR = $[CH_2]_4$

SCHEME 1

At the time of our original observation [3] there were few examples of 1,5-acyl migration, and no evidence regarding the concertedness or otherwise of the process. Accordingly we sought precedent for 1,5-acyl migration by studying the thermolysis of 1-acyl indenes (3; X = acyl). By analogy with the rearrangement of 1-arylindenes (3; X = Ar),[4] a 1-acylindene (3; X = acyl) might be expected to undergo a 1,5-acyl shift to a 2*H*-indene intermediate (4; X = acyl) which by a 1,5-hydrogen shift would give the 2-acylindene (5; X = acyl). It was hoped that a variety of 1-acylindenes could be readily prepared so that the migratory aptitudes of different acyl groups could be obtained by measuring



SCHEME 2

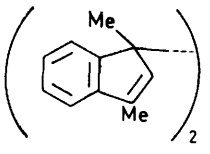
the overall rate of conversion of a 1-acylindene (3; X = acyl) to the 2-isomer (5; X = acyl). This would enable us to test for the concertedness of the 1,5-acyl shift and enquire into the apparently divergent migratory aptitudes of acyl and alkyl groups. Subsequent to our own [3] and contemporary [5] observations, the 1,5-acyl shift has emerged as an ubiquitous reaction type.[6] However evidence for the concerted nature of the process is sparse,[5a,6a] and in some cases a dissociation–recombination mechanism has been proposed.[6d] No explanation

[1] Part 12, D. W. Jones, *J.C.S. Perkin I*, 1977, 980.
[2] D. W. Jones and G. Kneen, *J.C.S. Perkin I*, 1975, 171.
[3] D. W. Jones and G. Kneen, *Chem. Comm.*, 1971, 1356.
[4] L. L. Miller and R. F. Boyer, *J. Amer. Chem. Soc.*, 1971, **93**, 650.
[5] (*a*) J. A. Berson and R. G. Solomon, *J. Amer. Chem. Soc.*, 1971, **93**, 4620; (*b*) R. A. Baylouny, *ibid.*, p. 4621.
[6] (*a*) P. Schiess and P. Fünfschilling, *Tetrahedron Letters*, 1972, 5191, 5195, and cited references; (*b*) C. P. Falshaw, S. A. Lane, and W. D. Ollis, *J.C.S. Chem. Comm.*, 1973, 491, and cited references; (*c*) M. Franck-Neumann and C. Buchecker, *Tetrahedron Letters*, 1972, 937; T. Yamazaki and H. Schechter, *ibid.*, p. 4533; (*d*) T. Yamazaki and H. Schechter, *ibid.*, 1973, 1417; T. Yamazaki, G. Baum, and H. Schechter, *ibid.*, 1974, 4421.

for the greater migratory aptitude of acyl than of alkyl groups has been advanced since we proposed [3] a homoconjugative interaction between the π-systems of the diene and migrating acyl group.

Preparation of 1-*Acyl*-1,3-*diphenyl- and* 1-*Acyl*-1,3-*dimethyl-indenes, and Related Compounds.*—Our first experiments involved the 1-methoxycarbonyl-1,3-diphenylindene (3; R = Ph, X = CO_2Me), for both it and its expected rearrangement product (5; R = Ph, X = CO_2Me) are known.[7a,b] However (3; R = Ph, X = CO_2Me), and the other 1-acylindenes used in our study were best prepared from 1,3-diphenyl- or 1,3-dimethyl-indene by conversion into the lithium salt with n-butyl-lithium followed by reaction with the appropriate acyl halide. The amide (3; R = Ph, X = CO·NHMe) was prepared from the corresponding methyl ester by reaction with methylamine. 1-Formyl-1,3-diphenylindene was prepared by oxidation (CrO_3–C_5H_5N–CH_2Cl_2) of the known [7c] alcohol (3; R = Ph, X = CH_2·OH), itself prepared by condensation of 1,3-diphenylindene with formalin in basic solution. 1-Formyl-1,3-dimethylindene was similarly prepared by reaction of the 1,3-dimethylindenide ion (Li salt) with gaseous formaldehyde and oxidation of the resulting alcohol.

1-Formyl-1,3-diphenylindene was converted into the related nitrile by dehydration of its oxime with acetic



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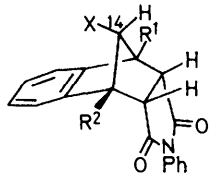


(7)

anhydride. The 1-formylindenes were converted into corresponding acetyl and benzoylindenes by Grignard reactions followed by oxidation of the resulting alcohols (CrO_3–C_5H_5N–CH_2Cl_2). The reaction of 1,3-dimethylindenyl-lithium with solid carbon dioxide gave the acid (3; R = Me, X = CO_2H), which was converted into the phenyl and *p*-nitrophenyl esters by reactions with phenol or *p*-nitrophenol in the presence of dicyclohexylcarbodi-imide. In the presence of 1,4-diazabicyclo-[2.2.2]octane, 1-methyl-3-phenylindenyl-lithium and acetyl chloride gave a 3.6 : 1 mixture of 1-acetyl-1-methyl-3-phenylindene and 1-acetyl-3-methyl-1-phenylindene. Quenching 1-methyl-3-phenylindenyl-lithium with methyl chloroformate gave a non-separable mixture of 1-methoxycarbonyl-1-methyl-3-phenylindene and 1-methoxycarbonyl-3-methyl-1-phenylindene in the ratio 8 : 1; quenching in the presence of diazabicyclo-octane changed this ratio to 3 : 2. An attempt to prepare [3; R = Me, X = CO·C_6H_4·NO_2(*p*)] by the reaction of 1,3-dimethylindenyl-lithium with *p*-nitrobenzoyl chloride resulted instead in an indene dimer tentatively formulated as (6); presumably oxidation of the indenide ion by the nitro-compound affords an indenyl radical which dimerises to (6).

Thermal Rearrangement of 1-*Acylindenes.*—The majority of the indenes (3; R = Ph, X = acyl) and (3; R = Me, X = acyl) underwent clean thermal rearrangement to the corresponding 2-acylindenes (5), demonstrating a uniform preference for acyl migration in competition with methyl and phenyl groups. In contrast 1-cyano-1,3-diphenylindene (3; R = Ph, X = CN) gave a 1 : 2.3 mixture of (5; R = Ph, X = CN) formed by migration of the cyano-group and 1-cyano-2,3-diphenylindene derived by phenyl migration; apparently the phenyl and cyano groups show similar migratory aptitudes at least when in direct competition. Rearrangement of 1-formyl-1,3-diphenylindene to the 2-isomer was accompanied by decarbonylation to 1,3-diphenylindene, but the base-catalysed reaction proceeded cleanly, as did the purely thermal rearrangement of 1-formyl-1,3-dimethylindene.

Mechanistic Studies.—The overall rate of the 1-acylindene (3) ⟶ 2-acylindene (5) conversion (k_{obs}) will only represent the migratory aptitude of the acyl group (k_1) if in the 2*H*-indene intermediate (4) reverse shift (k_{-1}) is slow compared with the forward-going hydrogen shift (k_2).* At the time of our first experiments only trimethylsilyl and related groups were known to migrate more rapidly than hydrogen,[8] so it appeared likely that k_{-1} would be less than k_2. However a number of experiments were performed to test the reversibility of both the first and the second steps of the sequence in Scheme 2. Although 1,3-diphenylindene (3; R = Ph; X = H) readily forms the adduct (7; R^1 = R^2 = Ph, X = H) of the 2*H*-indene (4; R = Ph, X = H) with *N*-phenylmaleimide at 140 °C, 2-formyl-1,3-diphenylindene is unchanged on heating with *N*-methylmaleimide at 160 °C. Since the 2*H*-indene (4; R = Ph, X = CHO) is readily trapped by *N*-phenylmaleimide at 70 °C (see below), a 2-formyl substituent must strongly retard migration of hydrogen to the 2-position. Heating 1-benzoyl-1,3-dimethylindene (1; R = Me, X = COPh) with *N*-phenylmaleimide at 170 °C gives the adduct (7; R^1 = R^2 = Me, X = COPh) derived from the 2*H*-indene formed by 1,5-benzoyl migration. However *N*-phenylmaleimide and 2-benzoyl-1,3-dimethylindene (5; R = Me, X = COPh) at 170 °C do not give this adduct. Accordingly it is unlikely that reversibility of the second step of Scheme 2 will be important at the temperatures used for initial rearrangement of these acyl groups.

Trapping experiments also provided information on the reversibility of the first step of Scheme 2. Thus although conversion of (3; R = Me, X = CHO) into the 2-isomer (5; R = Me, X = CHO) is slow below

* Assuming k_{-2} is unimportant, $k_{obs} = k_1k_2/(k_{-1} + k_2)$, so that $k_{obs} \approx k_1$ if $k_2 \gg k_{-1}$.

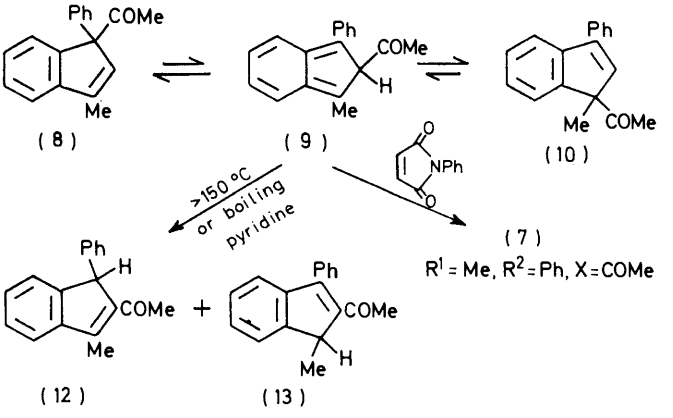
[7] (*a*) M. T. Goebel and C. S. Marvel, *J. Amer. Chem. Soc.*, 1933, **55**, 3712; (*b*) C. F. Koelsch, *J. Org. Chem.*, 1960, **25**, 2088; (*c*) 1961, 4238.

[8] A. J. Ashe, *J. Amer. Chem. Soc.*, 1970, **92**, 1233; *Tetrahedron Letters*, 1970, 2105; R. B. Larabee and B. F. Dowden, *ibid.*, p. 915; A. Davison and P. E. Rakita, *Inorg. Chem.*, 1970, **9**, 289.

200 °C (k 3.66 × 10^{-5} s^{-1} at 170 °C in Ph_2O), the adduct (7; $R^1 = R^2 = Me$, X = CHO) and a trace of its C-14 epimer were obtained (78% yield) by heating (3; R = Me, X = CHO) with *N*-phenylmaleimide at 80 °C (70 h). Similarly rearrangement of (3; R = Ph, X = CHO) is slow at 120 °C (k 1.64 × 10^{-5} s^{-1} at 120 °C in decalin) but the 2*H*-indene adduct of (4; $R^1 = R^2 = Ph$, X = CHO) can be prepared in high yield by heating 1-formyl-1,3-diphenylindene and *N*-phenylmaleimide at 70 °C. These experiments suggest that reverse formyl shift in the 2*H*-indene intermediates is much faster than the hydrogen shift leading to 2-acylindenes. Thus at temperatures below 150 °C the formyl group in (3; R = Me, X = CHO) is shuttled over C-1, C-2, and C-3 of the indene nucleus without noticeable formation of the 2-formylindene. This process exchanges the environments of the two methyl groups in (3; R = Me, X = CHO) and if sufficiently rapid would be observable in the n.m.r. spectrum. However the well separated methyl signals of (3; R = Me, X = CHO) (δ 1.43 and 2.18) show no broadening at 150 °C. N.m.r. experiments on transfer of non-equilibrium spin [9] do reveal exchange of the environments of the two methyl groups. At 150 °C a second radio frequency equal to the resonance frequency of the tertiary methyl group causes a 62% decrease in the intensity of the vinylic methyl signal. As expected the effect diminishes with temperature and the power of the second radiofrequency. This experiment indicates remarkably rapid formyl migration (k *ca.* 0.1 s^{-1} at 150 °C).

Since a phenyl group at the migration origin might be expected to accelerate migration,[4] formyl migration in (3; R = Ph, X = CHO) may proceed at room temperature. This could explain our earlier observation of a large solvent effect on the rearrangement of (3; R = Ph, X = CHO) to (5; R = Ph, X = CHO); rearrangement proceeds *ca.* 200 times more rapidly in dimethylformamide (DMF) (k 23.8 × 10^{-5} s^{-1} at 70 °C) than in decalin (k 1.64 × 10^{-5} s^{-1} at 120 °C). The dimethylamine usually present as an impurity in DMF might be sufficiently basic to remove the proton α to the formyl group in the 2*H*-indene (4; R = Ph, X = CHO) and thus catalyse conversion into the 2-formylindene. In accord with this explanation rearrangement of (3; R = Me, X = CHO) to its 2-isomer is only 3.6 times faster in DMF (k 13.15 × 10^{-5} s^{-1} at 170 °C) than in diphenyl ether (k 3.66 × 10^{-5} s^{-1} at 170 °C); the proton α to carbonyl in (4; R = Me, X = CHO) would be expected to be less acidic than that in the diphenyl-substituted 2*H*-indene. Further evidence for this explanation was provided by conducting the rearrangement of (3; $R^1 = R^2 = Ph$, X = CHO) in pyridine; conversion into the 2-formyl isomer was complete in 5 h at room temperature.

To test whether acetyl or hydrogen migration is more rapid in a 2*H*-indene intermediate (4), the unsymmetrically substituted indene (8) was prepared and its thermolysis studied. If acetyl migration were faster than hydrogen migration in the 2*H*-indene (9) (Scheme 3) conversion of (8) into (10) should be observed. Alternatively, more rapid migration of hydrogen than of acetyl in (9) would lead to a mixture of the 2-acetylindenes (12) and (13). Heating (8) at 110—140 °C led to clean and rapid conversion into isomer (10) (k 5.5 × 10^{-5} s^{-1} at 110 °C in diphenyl ether) strongly suggesting a more rapid shift of acetyl than of hydrogen in the 2*H*-indene (9). An alternative explanation for the conversion of (8) into (10) would be a direct 1,3-acetyl shift. However this is less likely, as the 2*H*-indene (9) can be intercepted by *N*-phenylmaleimide as the adduct (7; $R^1 = Me$, $R^2 = Ph$, X = COMe). Moreover the



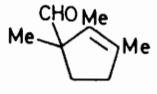
SCHEME 3

aldehyde (11) resists racemisation at 190 °C (12 h), suggesting that 1,3-acyl migration is not an easy process. The conversion of (8) into (10) is probably an equilibrium reaction strongly favouring (10), for the adduct (7; $R^1 = Me$, $R^2 = Ph$, X = COMe) is obtained by heating (10) with *N*-phenylmaleimide at 140 °C. At higher temperatures (>150 °C) the hydrogen shift in (9) competes with acetyl migration and the 2-acylindenes (12) and (13) are formed in the ratio *ca.* 1 : 3 (n.m.r. spectrum). The conversion of (8) into (12) and (13) is catalysed by pyridine. This presumably involves abstraction of the acidic proton α to the carbonyl group. Conversion of (3; R = Ph, X = COMe) into (5; R = Ph, X = COMe) is also accelerated in pyridine; the reaction proceeds slowly (k 4.99 × 10^{-5} s^{-1} at 140 °C) in diphenyl ether but is complete in 1.5 h at 116—118 °C in pyridine. The ratio of (12) to (13) formed in diphenyl ether (1 : 3) probably represents kinetic control of the hydrogen shift from C-2 in the 2*H*-indene (9). When rearrangement of (8) is conducted in pyridine (12) and (13) are found in the ratio 3 : 1, suggesting that (12) and (13) undergo base-catalysed interconversion and that (12) is the more stable isomer; this is confirmed by conversion of the 1 : 3 mixture of (12) and (13) into the 3 : 1 mixture in boiling pyridine. More ready conversion of (9) into (13) than into (12) may be due to a steric effect. The greater selectivity shown by the acetyl group in migrating almost exclusively towards the methyl rather than the phenyl group in (9) supports

[9] *Cf.* I. Calder, P. J. Garratt, and F. Sondheimer, *Chem. Comm.*, 1967, 41, and cited references.

steric control of the shifts from C-2. However in this case developing conjugation of the indene double bond with the phenyl substituent could also favour migration towards the methyl-bearing carbon atom. The greater stability of (12) than of (13) suggests that in (13) steric factors prevent full conjugation of the phenyl group with the enone system. Thus the conjugative effect should be less important in determining the direction of hydrogen than that of acetyl migration from C-2 of (9).

It is probable that, like formyl and acetyl migration, benzoyl migration is faster than hydrogen migration in the 2*H*-indene intermediates. Thus (4; R = Me, X = COPh) is readily intercepted as the adduct (7; R^1 = R^2 = Me, X = COPh) by heating (3; R = Me, X = COPh) with *N*-phenylmaleimide at 170 °C. Formation of the 2-benzoylindene also occurs at this temperature (k 18.9 × 10^{-5} s^{-1}), and reasonably efficient trapping of



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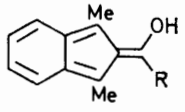

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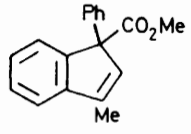

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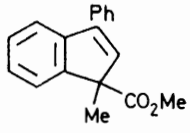


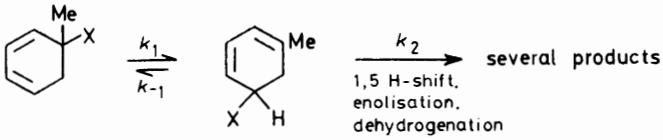
(16)

the 2*H*-indene would only be expected if it were formed reversibly from (3; R = Me, X = COPh).

Most rapid rearrangement of 1- to 2-acylindenes was observed for migrating benzoyl groups, *e.g.* for (3; R = Ph, X = COPh) k = 44.9 × 10^{-5} s^{-1} at 130 °C in diphenyl ether. This may in part be due to a more ready formation of the enol or enolate anion, *e.g.* (14), when R = Ph than when R = Me or hydrogen.

These experiments suggest that migration of formyl, acetyl, and benzoyl groups in the 2*H*-indenes (4) is more rapid than the competing hydrogen shifts from C-2. Accordingly migratory aptitudes for these groups (k_1 values) (Scheme 2) are not given by the rate constants for the overall conversions of (3) into (5). However, hydrogen migration appears to be more rapid than methoxycarbonyl migration in an intermediate of type (4). Thus a mixture of (15) and (16) (either 1 : 8 or 2 : 3) provides no evidence of interconversion of the isomers on heating up to the temperature resulting in formation of the 2-methoxycarbonylindenes (n.m.r.). Rate constants for the conversion of (3; R = Ph, X = CO_2Me) into (5; R = Ph, X = CO_2Me) therefore represent the rates of the initial methoxycarbonyl migration (k_1 values) and yield meaningful activation parameters [10^5 k/s^{-1} (T/°C)]: 3.13 (200), 8.91 (215), 24.1 (230), 37.3 (235), 56.7 (240); $\Delta H^{\ddagger}$ 33.34 ± 1.2 kcal mol^{-1}, $\Delta S^{\ddagger}$ −9.55 ± 2.74 cal K^{-1} mol^{-1}. Comparison of the data with those for rearrangement of 1,1,3-triphenylindene [4] indicates that methoxycarbonyl migration occurs *ca.* 3 times more rapidly than phenyl migration at 230 °C. The rate of rearrangement of (3; R = Ph, X = CO_2Me) is unchanged in the presence of hydroquinone or benzoyl peroxide, and is not accelerated by either benzoic acid or tributylamine. The failure of a radical trap (hydroquinone), a radical initiator (benzoyl peroxide), and acidic and basic catalysts to influence the rearrangement support a concerted methoxycarbonyl migration for the conversion of (3; R = Ph, X = CO_2Me) into the corresponding 2*H*-indene. Mechanisms involving initial cleavage of the indenyl–acyl bond to either radicals or ions therefore appear less likely. That free radicals are not involved is supported by our failure to observe CIDNP effects on heating (3; R = Me, X = CHO) to 150 °C, at which temperature reversible rearrangement to (4; R = Me, X = CHO) is rapid. Similarly when (3; R = Me, X = COPh) and (3; R = Ph, X = COMe) rearranged together, only the 2-isomers (5; R = Me, X = COPh or COMe), expected from intramolecular rearrangement, were detected (n.m.r. and t.l.c.).

Rearrangement of (3; R = Me, X = CO_2Me) is *ca.* 40 times slower (k 3.82 × 10^{-5} s^{-1} at 255 °C) than rearrangement of (3; R = Ph, X = CO_2Me). This agrees with the accelerating effect of 1- and 3-phenyl substituents on phenyl migration in related indenes.[4] In accord with implication of the π-system of the acyl group in the rearrangement transition state the phenyl ester (3; R = Me, X = CO_2Ph) rearranges 4.16 times more rapidly (k 15.9 × 10^{-5} s^{-1} at 255 °C) than the methyl ester, and the *p*-nitrophenyl ester [3; R = Me, X = CO_2·$C_6H_4NO_2$(*p*)] rearranges still faster (k 23.3 × 10^{-5} s^{-1} at 255 °C). A more detailed discussion of this



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SCHEME 4

point will be reserved for a subsequent paper; *para*-substituents also produce only small effects in migrating aryl groups where electron withdrawal again promotes rearrangement.[10] Whilst this work was in progress Schiess and Funfschilling [6a] described rearrangement of the cyclohexadienes (17; X = CHO, COMe, or CO_2Me) to the isomers (18) and thence to a variety of products (Scheme 4). They proposed an order of migratory aptitude CHO > COMe > H > CO_2Me identical with that deduced in this work, and fully confirmed by our study with optically active indenes (3; R = Me, X = acyl, *etc.*).[11] Overall rate constants provide an adequate measure of migratory aptitude in the cyclohexadiene system (17) but do not do so for the indene system (3).

[10] J. J. McCullough and M. R. McClory, *J. Amer. Chem. Soc.*, 1974, **96**, 1962.

[11] D. J. Field, D. W. Jones, and G. Kneen, unpublished results reported at the Chemical Society Congress, Leicester, September 1974.

In (4) and (18) the rate ratios for formyl to hydrogen migration are probably similar (bearing in mind the higher temperatures required for the cyclohexadienes). It seems likely that enolisation of (18) competes favourably with reverse formyl shift, but that in (4; X = CHO) the reverse formyl migration is much faster than enolisation. The transition state for the reverse formyl shift in the high energy intermediate (4) presumably reflects to some extent the aromatic stability of the product (3); the transition state for enolisation of (4) to (14) would not benefit in this way. In addition a rapid dehydrogenation of (18), impossible for (4), effectively increases the value of the k_2 term in the cyclohexadiene reaction (Scheme 4).

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. Unless otherwise specified i.r. spectra refer to Nujol mulls, and n.m.r. spectra to solutions in deuteriochloroform measured with a Varian A60A or Perkin-Elmer R12 B spectrometer. Mass spectra were obtained with an A.E.I. MS902 instrument. Petroleum refers to light petroleum (b.p. 60—80 °C) and chromatography on silica to short-column chromatography [12] over Kieselgel G (Merck).

Kinetic Measurements.—The indene (*ca.* 100 mg) was dissolved in the required solvent (0.3 ml), and pipetted into a clean, dry n.m.r. tube. The tube was immersed in an oil-bath previously stabilised at the required temperature (±1 °C). At regular intervals the tube was removed and immediately immersed in a cold-water bath. The n.m.r. spectra of the mixtures were measured with a Perkin-Elmer R12 B spectrometer. Each peak area in the n.m.r. spectrum was carefully integrated five times and an average integral calculated. All rearrangements were followed to at least 80% completion or about 2.5 half-lives. In all cases straight lines were obtained from rate plots. All slopes and intercepts were obtained from a least-squares program fed into a Seiko S 301 calculator.

1-*Hydroxymethyl*-1,3-*diphenylindene* (3; R = Ph, X = CH_2·OH).—This *alcohol* was prepared by the method of Koelsch [7c] from 1,3-diphenylindene,[13] and purified by chromatography on silica in ether–benzene (1 : 9) (Found: M^+, 298.135. $C_{22}H_{18}O$ requires M, 298.136), $\nu_{max.}$ (film) 3 490 cm^{-1}, δ 7.75—6.9 (14 H, m, aromatic), 6.62 (1 H, s), 3.99 (2 H, AB pattern, J 12 Hz), and 2.26br (1 H, s, OH).

1,3-*Diphenylindene*-1-*carbaldehyde* (3; R = Ph, X = CHO).—Chromium trioxide (9.0 g, 90 mmol) was added to pyridine (14.5 g, 180 mmol) in dichloromethane (250 ml) under nitrogen, and the resulting solution was stirred at 20 °C (15 min). The foregoing alcohol (4.2 g, 1.41 mmol) was added in the minimum quantity of dichloromethane. A tar immediately separated, and stirring was continued (1 h). The product was diluted with ether and washed with dilute sodium hydroxide solution (2×), dilute hydrochloric acid (2×), sodium hydrogen carbonate solution (2×), and brine (2×), dried ($MgSO_4$), and evaporated. Chromatography of the residue on silica in benzene gave the *aldehyde* (2.21 g, 53%), $\nu_{max.}$ 2 805, 2 710, and 1 710 cm^{-1}, δ 9.08 (1 H, s, CHO), 7.8—7.2 (14 H, m, aromatic), 6.58 (1 H, s, olefinic). The *oxime* had m.p. 173—176° (from benzene–petroleum) (Found: C, 85.1; H, 5.35; N, 4.4. $C_{22}H_{17}NO$ requires C, 84.9; H, 5.5; N, 4.5%), $\nu_{max.}$ 3 260 cm^{-1}, δ 8.46br (1 H, s, OH), 7.92 (1 H, s), 7.8—7.2 (14 H, m), and 6.65 (1 H, s).

1,3-*Diphenylindene*-1-*carbonitrile* (3; R = Ph, X = CN).—The foregoing oxime (450 mg) and acetic anhydride (3 ml) were boiled under reflux in nitrogen (45 min). Evaporation under reduced pressure on a water-bath and chromatography of the residue on silica in benzene gave the *nitrile* (291 mg, 72%), m.p. 80—82° (from benzene–petroleum) (Found: C, 90.25; H, 5.25; N, 5.1. $C_{22}H_{15}N$ requires C, 90.1; H, 5.15; N, 4.8%), $\nu_{max.}$ 2 220 cm^{-1}, δ 7.8—7.1 (14 H, m) and 6.49 (1 H, s).

1-*Benzoyl*-1,3-*diphenylindene*.—Phenylmagnesium bromide (200 mg, 1.1 mmol) [from magnesium (0.6 g) and bromobenzene (3.92 g), and standardised at 65 mg PhMgBr per ml] was added in dry ether to the foregoing aldehyde (296 mg, 1 mmol) in dry ether, under nitrogen. The mixture was stirred at 20 °C (1 h), and poured into ammonium chloride solution. The product was extracted into ether; the extract was washed with water, dried ($MgSO_4$), and evaporated. A portion (68 mg) of the residual oil (368 mg) was chromatographed on silica in benzene to give the *alcohol* (3; R = Ph, X = PhCHOH) (61 mg) (Found: M^+, 374.165. $C_{28}H_{22}O$ requires M, 374.167), $\nu_{max.}$ 3 400 cm^{-1}, δ 7.8—6.9 (19 H, m), 6.85 (1 H, s), 5.67br (1 H, s), and 2.37br (1 H, s, OH). The alcohol (300 mg) was oxidised with chromium trioxide (600 mg) and pyridine (950 mg) in methylene chloride (15 ml) as described above, to give 1-*benzoyl*-1,3-*diphenylindene* (266 mg, 89%), m.p. 151—153° (from benzene–petroleum) (Found: C, 90.3; H, 5.6. $C_{28}H_{20}O$ requires C, 90.3; H, 5.4%), $\nu_{max.}$ 1 681 cm^{-1}, δ 7.8—7.1 (19 H, m) and 6.85 (1 H, s).

1-*Acetyl*-1,3-*diphenylindene* (3; R = Ph, X = COMe).—Methylmagnesium iodide (185 mg, 1.1 mmol) [from magnesium (0.6 g) and methyl iodide (3.55 g), and standardised at 62 mg MeMgI per ml] was added in dry ether to 1,3-diphenylindene-1-carbaldehyde (296 mg, 1.0 mmol) in dry ether, under nitrogen. The mixture was stirred at 20 °C (1 h) and poured into ammonium chloride solution. The product was extracted into ether, and the extract washed with water, dried ($MgSO_4$), and evaporated to give the *alcohol* (3; R = Ph, X = MeCHOH) (307 mg), which was purified by silica chromatography in benzene (Found: M^+, 312.151. $C_{23}H_{20}O$ requires M, 312.151), $\nu_{max.}$ (film) 3 430 cm^{-1}, δ 7.9—7.1 (14 H, m), 6.84 and 6.57 (total 1 H, two s, olefinic H in two diastereoisomers), 4.83 (1 H, m), 1.83br (1 H, s, OH), and 1.00 and 0.94 (3 H, two d, J 6 Hz, Me in two diastereoisomers). The alcohol (250 mg) was oxidised with chromium trioxide (600 mg) and pyridine (950 mg) in dichloromethane (15 ml) as described above. This gave 1-*acetyl*-1,3-*diphenylindene* (240 mg, 96%), m.p. 77—79° (from petroleum) (Found: C, 88.9; H, 5.75. $C_{23}H_{18}O$ requires C, 89.0; H, 5.8%), $\nu_{max.}$ 1 709 cm^{-1}, δ 7.8—7.1 (14 H, m), 6.7 (1 H, s), and 2.04 (3 H, s).

1,3-*Diphenylinden*-1-*yl-lithium*.—Butyl-lithium in hexane (4.0 ml of 2.5M; 10 mmol) was syringed into 1,3-diphenylindene (2.68 g, 10 mmol) in ether (65 ml) at 0—5 °C under nitrogen. The solution was stirred at *ca.* 20 °C (10 min) prior to quenching as described below.

(i) *Quenching with methyl chloroformate.* Methyl chloroformate (2 g) was added to the 1,3-diphenylindenyl-lithium and the mixture was stirred at room temperature (15 min). The product was washed with water, dried ($MgSO_4$), and evaporated, and the residue chromatographed on silica in benzene–petroleum (4 : 1) to give methyl 1,3-diphenylindene-1-carboxylate (3.0 g, 92%), m.p. 99—100° (lit.,[7a]

[12] B. J. Hunt and W. Rigby, *Chem. and Ind.*, 1967, 1868.
[13] K. Ziegler, H. Grabbe, and F. Ulrich, *Ber.*, 1924, **57**, 1988.

99—100°) (from ethyl acetate–methanol), $\nu_{max.}$ 1 722 cm^{-1}, $\lambda_{max.}$ 274.5 nm (ε 5 621), δ 7.85—7.1 (14 H, m), 6.77 (1 H, s), and 3.77 (3 H, s).

(ii) *Quenching with benzoyl chloride.* Benzoyl chloride (1.5 g, 1.07 mmol) was added to 1,3-diphenylindenyl-lithium to give 1-benzoyl-1,3-diphenylindene (3.0 g, 80%) identical (mixed m.p. and i.r. spectrum) with a sample previously prepared.

(iii) *Quenching with acetyl chloride.* Acetyl chloride (1.5 g) was added to 1,3-diphenylindenyl-lithium to give 1-acetyl-1,3-diphenylindene (2.4 g, 77%), identical with the sample previously prepared.

1,3-*Diphenylindene*-1-N-*methylcarboxamide* (3; R = Ph, X = CONHMe).—Methyl 1,3-diphenylindene-1-carboxylate (3.0 g) and methylamine (45 ml) were kept in sealed tubes (3 weeks). Evaporation left the *amide* (1.75 g, 58%), m.p. 201—204° (from benzene–petroleum) (Found: C, 85.1; H, 6.25; N, 4.6. $C_{23}H_{19}NO$ requires C, 84.9; H, 5.9; N, 4.3%), $\nu_{max.}$ 3 320 and 1 642 cm^{-1}, δ 7.8—7.0 (14 H, m), 6.73 (1 H, s), and 2.77 (3 H, d, *J* 4.5 Hz).

1,3-*Dimethylinden*-1-*yl-lithium*.—Butyl-lithium in hexane (2.8 ml of 2.5M; 7.0 mmol) was syringed into 1,3-dimethylindene [14] (1.0 g, 7.0 mmol) at 0—5 °C under nitrogen. The solution soon deposited the salt, and the slurry was stirred at room temperature (10 min) prior to quenching as follows.

(i) Addition of methyl chloroformate (1.0 g), stirring at room temperature (15 min), washing with water, drying ($MgSO_4$), and evaporation gave *methyl* 1,3-*dimethylindene*-1-*carboxylate* (3; R = Me, X = CO_2Me), which was purified by silica chromatography in benzene–petroleum (4 : 1) (1.03 g, 74%) (Found: M^+, 202.099. $C_{13}H_{14}O_2$ requires *M*, 202.099), $\nu_{max.}$ 1 734 cm^{-1}, $\lambda_{max.}$ 259 nm (ε 6 355), δ 7.5—6.8 (4 H, m), 6.07 (1 H, q, *J* 1.5 Hz), 3.47 (3 H, s), 2.08 (3 H, d, *J* 1.5 Hz), and 1.51 (3 H, s).

(ii) Benzoyl chloride (2.0 g) was added to 1,3-dimethylindenyl-lithium [from 1,3-dimethylindene (1.44 g) and butyl-lithium (42 ml; 2.5M in hexane)], and the product was worked up as described in (i), to give 1-*benzoyl*-1,3-*dimethylindene* (3; R = Me, X = COPh) (1.74 g, 70%) after purification by silica chromatography in benzene, m.p. 72.5—74° (from petroleum at 0 °C) (Found: C, 87.3; H, 6.4. $C_{18}H_{16}O$ requires C, 87.1; H, 6.5%), $\nu_{max.}$ 1 675 cm^{-1}, δ 7.5—7.0 (9 H, m), 6.23 (1 H, q, *J* 1.5 Hz), 2.18 (3 H, d, *J* 1.5 Hz), and 1.61 (3 H, s).

(iii) Paraformaldehyde (18 g; vacuum-dried over P_2O_5) was heated at 180—200 °C in a slow nitrogen stream, and the formaldehyde gas so formed was passed over a stirred slurry of 1,3-dimethylindenyl-lithium [from butyl-lithium (10 ml of 2.5M in hexane) and 1,3-dimethylindene (3.6 g)]. The product was washed with ammonium chloride, dried ($MgSO_4$), and evaporated to give 1-*hydroxymethyl*-1,3-*dimethylindene* (3; R = Me, X = CH_2OH) (4.05 g, 93%) (Found: M^+, 174.104. $C_{12}H_{14}O$ requires *M*, 174.104), $\nu_{max.}$ 3 380 cm^{-1}, δ 7.5—7.0 (4 H, m), 6.00 (1 H, q, *J* 1.5 Hz), 3.54br (2 H, s), 2.07 (3 H, d, *J* 1.5 Hz), 1.26 (3 H, s), and 2.15br (1 H, s, OH).

(iv) A slurry of 1,3-dimethylindenyl-lithium [from 1,3-dimethylindene (1 g) and butyl-lithium (2.8 ml of 2.5M in hexane)] was poured with stirring onto a slurry of solid carbon dioxide in ether. The mixture was allowed to warm to room temperature and extracted with sodium hydrogen carbonate solution. Acidification of the extracts, extraction into ether, drying of the ethereal solution ($MgSO_4$), and evaporation gave 1,3-*dimethylindene*-1-*carboxylic acid* (3; R = Me, X = CO_2H) (980 mg, 75%), m.p. 116—120° (from petroleum) (Found: C, 76.5; H, 6.5. $C_{12}H_{12}O_2$ requires C, 76.6; H, 6.4%), $\nu_{max.}$ 1 686 cm^{-1}, δ 9.94br (1 H, s, OH), 7.6—7.1 (4 H, m), 6.15 (1 H, q, *J* 1.5 Hz), 2.11 (3 H, d, *J* 1.5 Hz), and 1.57 (3 H, s). With diazomethane the acid gave the methyl ester, identical (n.m.r.) with that already described.

(v) Excess of *p*-nitrobenzoyl chloride in ether was added to 1,3-dimethylindenyl-lithium [from butyl-lithium (2.8 ml of 2.5M in hexane) and 1,3-dimethylindene (1 g)]. The mixture was stirred at *ca.* 20 °C (30 min), washed with water, dried ($MgSO_4$), and evaporated to give an oil (1.5 g) containing *p*-nitrobenzoyl chloride. Preparative layer chromatography of a portion (60 mg) on silica in benzene–petroleum (1 : 9) gave the diastereoisomeric 1,1′,3,3′-*tetramethyl*-1,1′-*bi-indenes* (6) (30 mg), m.p. 121—133° (from chloroform–ethanol) (Found: C, 92.0; H, 7.5. $C_{22}H_{22}$ requires C, 92.3; H, 7.7%), δ 7.4—6.8 (8 H, m), 6.12 and 5.93 (1 H, two q, *J* 1.5 Hz, *meso* and racemic forms), 2.04 and 2.00 (3 H, two d, *J* 1.5 Hz), and 1.39 and 1.19 (3 H, two s).

1,3-*Dimethylindene*-1-*carbaldehyde* (3; R = Me, X = CHO).—1-Hydroxymethyl-1,3-dimethylindene (3.75 g, 21.6 mmol) was oxidised with chromium trioxide (13.2 g, 132 mmol) and pyridine (20.85 g, 264 mmol) in dichloromethane (250 ml) as described for the 1,3-diphenyl analogue, except that a mechanical stirrer was used and the chromium trioxide was added to the pyridine–dichloromethane at 0—5 °C. After the usual work-up, chromatography on silica in benzene gave the *aldehyde* (2.95 g, 81%) (Found: M^+, 172.089. $C_{12}H_{12}O$ requires *M*, 172.089), $\nu_{max.}$ 1 714 cm^{-1}, δ 8.45 (1 H, s), 7.5—7.1 (4 H, m), 5.88 (1 H, q, *J* 1.5 Hz), 2.18 (3 H, d, *J* 1.5 Hz), and 1.43 (3 H, s).

Reduction of 1,3-*Dimethylindene*-1-*carboxylic Acid with Lithium Aluminium Hydride*.—The indene (1.88 g, 10 mmol) in dry ether (15 ml) was cooled to −15 to −20 °C (CCl_4–solid CO_2 bath) under nitrogen, and lithium aluminium hydride (550 mg) was added in small portions over a few minutes. The mixture was stirred at −15 to −20 °C (1 h) and then at *ca.* 20 °C (30 min). The product was isolated by dropwise addition of water with cooling followed by dilute sulphuric acid. Evaporation of the dried ($MgSO_4$) ether layer gave 1-hydroxymethyl-1,3-dimethylindene (1.70 g), identical with the sample described previously (i.r. spectrum).

Conversion of 1,3-*Dimethylindene*-1-*carbaldehyde into* 1-*Benzoyl*-1,3-*dimethylindene*.—Phenylmagnesium bromide (200 mg, 1.1 mmol) [from bromobenzene (3.92 g) and magnesium (0.6 g), and standardised at 70 mg PhMgBr per ml] was added dropwise to an ethereal solution of the aldehyde (172 mg, 1 mmol), and the product (3; R = Me, X = PhCHOH) (230 mg, 92%) was isolated in the usual way; $\nu_{max.}$ 3 390 cm^{-1}. This alcohol (230 mg) was oxidised with chromium trioxide (600 mg) and pyridine (949 mg) in dichloromethane (15 ml) as before to give 1-benzoyl-1,3-dimethylindene (200 mg, 88%), identical with the sample already described (i.r. spectrum).

Conversion of 1,3-*Dimethylindene*-1-*carbaldehyde into* 1-*Acetyl*-1,3-*dimethylindene*.—Methylmagnesium iodide (100 mg, 0.62 mmol) [from magnesium (0.6 g) and methyl iodide (3.55 g), and standardised at 77 mg MeMgI per ml] was added dropwise to an ethereal solution of the aldehyde (86 mg, 0.5 mmol). Aqueous work-up gave the alcohol (3; R = Me, X = MeCHOH) (90 mg, 96%), $\nu_{max.}$ 3 390 cm^{-1}.

[14] *Cf.* L. Ohlsson, I. Wallmark, and G. Bergson, *Acta Chem. Scand.*, 1966, **20**, 750.

This alcohol (90 mg) was oxidised with chromium trioxide (600 mg) and pyridine (949 mg) in dichloromethane (10 ml) as before to give 1-*acetyl*-1,3-*dimethylindene* (83 mg, 89%) after silica chromatography in benzene (Found: M^+, 186.104. $C_{13}H_{14}O$ requires M, 186.104), $\nu_{max.}$ (film) 1 705 cm^{-1}, δ 7.5—7.2 (4 H, m), 6.06 (1 H, q, J 1.5 Hz), 2.21 (3 H, d, J 1.5 Hz), 1.62 (3 H, s), and 1.43 (3 H, s).

Phenyl 1,3-*Dimethylindene*-1-*carboxylate*.—1,3-Dimethylindene-1-carboxylic acid (94 mg, 0.5 mmol), phenol (47 mg, 0.5 mmol), and dicyclohexylcarbodi-imide (120 mg, 0.58 mmol) in acetonitrile (5 ml) were warmed on a water-bath (2 min) and kept at *ca.* 20 °C (1 h). Chromatography of the product on silica in benzene gave the *ester* (3; R = Me, X = CO_2Ph) (27 mg, 20.5%), m.p. 63—67° (from petroleum at 0 °C) (Found: C, 81.8; H, 6.0. $C_{18}H_{16}O_2$ requires C, 81.8; H, 6.1%), $\nu_{max.}$ 1 744 cm^{-1}, δ 7.7—6.5 (9 H, m), 6.26 (1 H, q, J 1.5 Hz), 2.12 (3 H, d, J 1.5 Hz), and 1.69 (3 H, s).

p-*Nitrophenyl* 1,3-*Dimethylindene*-1-*carboxylate*.—1,3-Dimethylindene-1-carboxylic acid (94 mg, 0.5 mmol), *p*-nitrophenol (70 mg, 0.5 mmol), and dicyclohexylcarbodiimide (120 mg, 0.58 mmol) in acetonitrile (5 ml) were treated as for the preparation of (3; R = Me, X = CO_2Ph). Silica chromatography in benzene gave the *ester* [3; R = Me, X = $CO_2{\cdot}C_6H_4{\cdot}NO_2(p)$] (130 mg, 84%), m.p. 84—86° (from ethanol) (Found: C, 69.8; H, 4.75; N, 4.4. $C_{18}H_{15}NO_4$ requires C, 69.9; H, 4.9; N, 4.5%), $\nu_{max.}$ 1 747 cm^{-1}, δ 8.19 (2 H, d, J 9.5 Hz), 7.7—7.0 (6 H, m), 6.28 (1 H, q, J 1.5 Hz), 2.18 (3 H, d, J 1.5 Hz), and 1.7 (3 H, s).

1-*Acetyl*-1-*methyl*-3-*phenyl*- *and* 1-*Acetyl*-3-*methyl*-1-*phenyl*-*indene*.—n-Butyl-lithium (6.2 ml of 2.03M in hexane) was syringed into a stirred mixture of 1-methyl-3-phenylindene [15] (2.5 g), 1,4-diazabicyclo[2.2.2]octane (1.4 g, 12.5 mmol), and tetrahydrofuran (136 ml) at *ca.* 20 °C under nitrogen, and the solution was stirred at *ca.* 20 °C (15 min) before introduction of acetyl chloride (1.2 g). After stirring (15 min) and washing with water the product was dried ($MgSO_4$) and evaporated, and the residue chromatographed on silica in benzene–petroleum (9 : 1) to give first 1-*acetyl*-1-*methyl*-3-*phenylindene* (10) (1.5 g, 50%) (Found: M^+, 248.120. $C_{18}H_{16}O$ requires M, 248.120), $\nu_{max.}$ 1 712 cm^{-1}, δ 7.8—7.2 (9 H, m), 6.39 (1 H, s), 1.7 (3 H, s), and 1.56 (3 H, s), and then 1-*acetyl*-3-*methyl*-1-*phenylindene* (8) (420 mg, 14%) (Found: M^+, 248.120), $\nu_{max.}$ 1 708 cm^{-1}, δ 7.6—7.1 (9 H, m), 6.31 (1 H, q, J 1.5 Hz), 2.2 (3 H, d, J 1.5 Hz), and 1.96 (3 H, s).

Reaction of 1-*Methyl*-3-*phenylindenyl-lithium with Methyl Chloroformate*.—Butyl-lithium (1.27 ml of 2.03M in hexane) was syringed into a stirred mixture of 1-methyl-3-phenylindene (512 mg, 2.0 mmol), 1,4-diazabicyclo[2.2.2]octane (287 mg, 2.56 mmol), and tetrahydrofuran (50 ml) at *ca.* 20 °C under nitrogen. The solution was stirred at *ca.* 20 °C (15 min), and methyl chloroformate (1 g) added. The product was washed with water, dried ($MgSO_4$), and evaporated, and the residue chromatographed on silica in benzene to give a mixture of the esters (15) and (16) (*ca.* 0.5 g) in the ratio 2 : 3. When the reaction was conducted in the absence of diazabicyclo-octane the esters (15) and (16) were formed in the ratio 1 : 8 (90% yield). Methyl 1-methyl-3-phenylindene-1-carboxylate (16) showed δ 7.75—7.1 (9 H, m). 6.49 (1 H, s), 3.56 (3 H, s), and 1.62 (3 H, s). The 3-methyl-1-phenyl isomer (15) showed δ 7.75—7.1 (9 H, m), 6.32 (1 H, m), 3.64 (3 H, s), and 2.08 (3 H, d, J 1.5 Hz). The mixture of isomers showed $\nu_{max.}$ 1 730 cm^{-1}.

[15] *Cf.* V. Bertoli and P. H. Plesch, *J. Chem. Soc.* (*B*), 1968, 1500.

Preparative Thermolysis of 1-*Acylindenes*.—(i) Methyl 1,3-diphenylindene-1-carboxylate (50 mg) and xylene (5 ml) were heated in a sealed tube (Carius oven) (12 h). Evaporation gave methyl 1,3-diphenylindene-2-carboxylate in quantitative yield, identical (i.r. and n.m.r. spectra) with an authentic sample,[7b,16] $\nu_{max.}$ (film) 1 711 cm^{-1}, δ 7.6—7.1 (14 H, m), 5.05 (1 H, s), and 3.48 (3 H, s).

(ii) 1,3-Diphenylindene-1-carbonitrile (40 mg) and xylene (3 ml) were treated as in (i). Chromatography of the product on silica in benzene–petroleum (4 : 1) gave 2,3-*diphenylindene*-1-*carbonitrile* (25 mg, 62.5%), m.p. 134—137° (from chloroform–ethanol) (Found: C, 89.95; H, 5.2; N, 4.75. $C_{22}H_{15}N$ requires C, 90.1; H, 5.15; N, 4.8%), $\lambda_{max.}$ 238 and 324 nm (ε 13 050 and 14 880), δ 7.9—6.8 (14 H, m) and 5.18 (1 H, s). Further elution gave 1,3-*diphenylindene*-2-*carbonitrile* (11 mg, 27.5%), m.p. 103—106° (from benzene–petroleum) (Found: C, 90.25; H, 5.4; N, 4.7%), $\lambda_{max.}$ 237, 263, and 299 nm (ε 26 790, 9 580, and 10 770), δ 7.9—6.9 (14 H, m) and 4.91 (1 H, s).

(iii) 1-Benzoyl-1,3-diphenylindene (60 mg) and xylene (3 ml) were treated as in (i) to give 2-benzoyl-1,3-diphenylindene (56 mg, 93%), m.p. 145—147° (lit.,[7c] 145—146°) (from benzene–petroleum), $\nu_{max.}$ 1 642 cm^{-1}, $\lambda_{max.}$ 235, 257, and 324 nm (ε 18 450, 11 750, and 8 420), δ 7.7—6.8 (19 H, m) and 5.36 (1 H, s).

(iv) 1,3-Diphenylindene-1-*N*-methylcarboxamide (60 mg) and xylene (6 ml) were treated as in (i) to give 1,3-*diphenylindene*-1-N-*methylcarboxamide* (55 mg, 91%), m.p. 185—187° (from benzene–petroleum) (Found: C, 84.85; H, 5.8; N, 4.1. $C_{23}H_{19}NO$ requires C, 84.9; H, 5.9; N, 4.3%). $\nu_{max.}$ 3 320 and 1 630 cm^{-1}, δ 7.49 (4 H, s), 7.22 (10 H, m), 5.2br (1 H, s), 5.1 (1 H, s), and 2.49 (3 H, d, J 5 Hz).

(v) Methyl 1,3-dimethylindene-1-carboxylate (100 mg) and xylene (5 ml) were treated as in (i) to give *methyl* 1,3-*dimethylindene*-2-*carboxylate* in quantitative yield (Found: M^+, 202.099. $C_{13}H_{14}O_2$ requires M, 202.100), $\nu_{max.}$ 1 705 cm^{-1}, δ 7.7—7.1 (4 H, m), 4.0—3.5 (4 H, m, including OMe at 3.83), 2.5 (3 H, d, J 2.2 Hz), and 1.38 (3 H, d, J 7.5 Hz).

(vi) 1-Acetyl-1,3-diphenylindene (50 mg) and xylene (3 ml) were treated at 220 °C as in (i) to give 2-*acetyl*-1,3-*diphenylindene* in quantitative yield (Found: M^+, 310.136. $C_{23}H_{18}O$ requires M, 310.135), $\nu_{max.}$ 1 658 cm^{-1}, δ 7.6—7.0 (14 H, m), 5.11 (1 H, s), and 1.88 (3 H, s).

(vii) 1-Benzoyl-1,3-dimethylindene (120 mg) and diphenyl ether (0.3 ml) were heated at 200 °C (45 min). Chromatography on silica in benzene gave 2-*benzoyl*-1,3-*dimethylindene* (115 mg, 96%), m.p. 55—58° (from benzene–petroleum) (Found: C, 87.05; H, 6.45. $C_{18}H_{16}O$ requires C, 87.1; H, 6.5%), $\nu_{max.}$ 1 635 cm^{-1}, $\lambda_{max.}$ 246, 255, and 318.5 nm (ε 11 000, 10 450, and 13 450), δ 8.0—7.65 (2 H, m), 7.65—7.2 (7 H, m), 4.1 (1 H, qd, J 2 and 7.5 Hz), 2.04 (3 H, d, J 2 Hz), and 1.35 (3 H, d, J 7.5 Hz).

(viii) 1,3-Dimethylindene-1-carbaldehyde (100 mg) and xylene (4 ml) were heated at 220 °C as in (i). Chromatography of the product on silica in benzene gave 1,3-*dimethylindene*-2-*carbaldehyde* (75 mg, 75%) (Found: M^+, 172.089. $C_{12}H_{12}O$ requires M, 172.089), $\nu_{max.}$ 1 656 cm^{-1}, δ 7.7—6.9 (4 H, m), 3.75 (1 H, qd, J 2 and 7.5 Hz), 2.48 (3 H, d, J 2 Hz), and 1.38 (3 H, d, J 7.5 Hz).

(ix) Phenyl 1,3-dimethylindene-1-carboxylate (30 mg) and diphenyl ether (0.5 ml) were heated at 255 °C (6 h), and the product was chromatographed on silica in benzene to give *phenyl* 1,3-*dimethylindene*-2-*carboxylate* (27 mg, 90%),

[16] J. M. Holland and D. W. Jones, unpublished data.

m.p. 62—65° (from petroleum at −20 °C) (Found: C, 82.0; H, 6.0. $C_{17}H_{16}O_2$ requires C, 81.8; H, 6.1%), $\nu_{max.}$ 1 711 cm^{-1}, δ 7.7—7.0 (9 H, m), 5.9 (1 H, qd, *J* 2 and 7.5 Hz), 2.59 (3 H, d, *J* 2 Hz), and 1.54 (3 H, d, *J* 7.5 Hz).

(x) *p*-Nitrophenyl 1,3-dimethylindene-1-carboxylate (80 mg) and diphenyl ether (0.4 ml) were heated at 255 °C (6 h) and the product was chromatographed on silica in benzene to give p-*nitrophenyl* 1,3-*dimethylindene*-2-*carboxylate* (20 mg, 25%), m.p. 120—122° (from ethanol) (Found: C, 69.6; H, 4.95; N, 4.3. $C_{18}H_{15}NO_4$ requires C, 69.9; H, 4.9; N, 4.5%), $\nu_{max.}$ 1 727 cm^{-1}, δ 8.33 (2 H, d, *J* 9.5 Hz), 7.7—7.2 (6 H, m), 3.85 (1 H, m), 2.63 (3 H, d, *J* 2 Hz), and 1.54 (3 H, d, *J* 7.5 Hz).

(xi) 1-Acetyl-3-methyl-1-phenylindene (50 mg) and diphenyl ether (0.3 ml) were heated at 150 °C (1 h) and the product was chromatographed on silica in benzene to give 1-acetyl-1-methyl-3-phenylindene, identical (i.r. and n.m.r. spectra) with material already described. Prolonged heating at this temperature produced no further change but at 200 °C (3 h) conversion into (12) and (13) in the ratio 1 : 3 was observed (n.m.r.).

(xii) 1,3-Diphenylindene-1-carbaldehyde (60 mg) and xylene (5 ml) were boiled under reflux in nitrogen (11 h). Evaporation and chromatography on silica in benzene–petroleum (9 : 1) gave 1,3-diphenylindene (27.5 mg, 46%), identical with an authentic sample (mixed m.p. and i.r. spectrum). Further elution gave 1,3-diphenylindene-2-carbaldehyde [17] (29 mg, 48.5%), $\nu_{max.}$ 1 656 cm^{-1}, δ 9.87 (1 H, s), 7.7—7.0 (14 H, m) and 5.03 (1 H, s). The *oxime* had m.p. 210—214° (from benzene–petroleum) (Found: C, 84.75; H, 5.35; N, 4.45. $C_{22}H_{17}NO$ requires C, 84.9; H, 5.5; N, 4.5%).

Catalysed Conversion of 1-*Acyl- into* 2-*Acyl-indenes*.—(i) 1,3-Diphenylindene-1-carbaldehyde (100 mg) and dimethylformamide (2 ml) were heated at 70 °C in nitrogen (4 h). Evaporation left 1,3-diphenylindene-2-carbaldehyde (95 mg), identical with an authentic sample (i.r. and n.m.r. spectra). A solution of the 1-aldehyde in pyridine undergoes *ca.* 50% conversion into the 2-isomer in 20 min, and complete conversion in 5 h.

(ii) 1-Acetyl-1,3-diphenylindene was completely converted into the 2-isomer after 1.5 h reflux in boiling pyridine.

(iii) 1-Acetyl-1-methyl-3-phenylindene (450 mg) and pyridine (8 ml) were boiled under reflux (24 h). Evaporation and chromatography of the product on silica in benzene–petroleum (9 : 1) gave starting material (30 mg), followed by 2-*acetyl*-1-*methyl*-3-*phenylindene* (13) (95 mg) (Found: M^+, 248.120. $C_{18}H_{16}O$ requires *M*, 248.119), $\nu_{max.}$ 1 650 and 1 620 cm^{-1}, δ 1.48 (3 H, d, *J* 7 Hz), 1.96 (3 H, s), 4.01 (1 H, q, *J* 7 Hz), 7.0—7.8 (9 H, m), and then 2-*acetyl*-3-*methyl*-1-*phenylindene* (12) (285 mg), m.p. 87—90° (from ethanol) (Found: C, 87.2; H, 6.5. $C_{18}H_{16}O$ requires C, 87.1; H, 6.5%), $\nu_{max.}$ 1 660, 1 600, and 1 590 cm^{-1}, δ 2.1 (3 H, s), 2.58 (3 H, d, *J* 2 Hz), 4.8 (1 H, q, *J* 2 Hz), and 6.9—7.7 (9 H, m). 1-Acetyl-3-methyl-1-phenylindene was largely converted into a mixture of (12) and (13) in the same proportions in boiling pyridine over 6 h. A mixture of (12) and (13) (ratio 1 : 3) was converted into the 3 : 1 in boiling pyridine over 2 h [t.l.c. on silica in benzene–petroleum (9 : 1) with double elution].

Trapping of Intermediate 2H-*Indenes* (4) *with Maleimides*.—(i) 1,3-Diphenylindene (268 mg, 1 mmol), *N*-methylmaleimide (166 mg, 1.5 mmol), and xylene (5 ml) were boiled under reflux in nitrogen (15 h). Evaporation gave the endo-*adduct* (7; $R^1 = R^2 = Ph$, X = H) (307 mg, 81%), m.p. 243—245° (from chloroform–petroleum) (Found: C, 82.0; H, 5.5; N, 3.5. $C_{26}H_{21}NO_2$ requires C, 82.3; H, 5.6; N, 3.7%), $\nu_{max.}$ 1 763 and 1 689 cm^{-1}, δ 8.1—6.7 (14 H, m), 4.1 (2 H, s), 3.0 (1 H, d, *J* 9.5 Hz), 2.45 (1 H, d, *J* 9.5 Hz), and 2.37 (3 H, s).

(ii) 1,3-Diphenylindene-1-carbaldehyde (156 mg), *N*-phenylmaleimide (43.2 mg), and acetonitrile (6 ml) were heated at 73—76 °C (3 days). Chromatography of the product on silica in ether–benzene (2 : 98) gave the *adduct* (7; $R^1 = R^2 = Ph$, X = CHO) (200 mg), m.p. 243—245° (from chloroform–ethanol) (Found: C, 82.15; H, 4.85; N, 2.8. $C_{32}H_{23}NO_3$ requires C, 81.9; H, 4.9; N, 3.0%), δ 3.29 (1 H, d, *J* 5.5 Hz), 4.23 (2 H, s), 6.47 (2 H, m), 7.0—7.8 (17 H, m), and 9.45 (1 H, d, *J* 5.5 Hz).

(iii) 1,3-Dimethylindene-1-carbaldehyde (100 mg), *N*-phenylmaleimide (300 mg), and diphenyl ether (2 ml) were heated at 80 °C (70 h). Chromatography on silica in benzene–ether (9 : 1) gave the syn,endo-*adduct* [C-14 epimer of (7; $R^1 = R^2 = Me$, X = CHO)] (7 mg, 3%), m.p. 171—175° (from chloroform–ethanol) (Found: M^+, 345.136. $C_{22}H_{19}NO_3$ requires *M*, 345.136), $\nu_{max.}$ 1 781 and 1 713 cm^{-1}, δ (90 MHz) 9.94 (1 H, d, *J* 2 Hz), 7.27 (7 H, m), 6.42 (2 H, m), 3.6 (2 H, s), 2.89 (1 H, d, *J* 2 Hz), and 9.89 (6 H, s). Further elution gave the anti,endo-*adduct* (7; $R^1 = R^2 =$ Me, X = CHO) (150 mg, 75%), m.p. 232—236° (from chloroform–ethanol) (Found: C, 76.35; H, 5.7; N, 4.05%), $\nu_{max.}$ 1 781 and 1 716 cm^{-1}, δ [$(CD_3)_2SO$] 9.19 (1 H, d, *J* 3.5 Hz), 7.5—7.1 (7 H, m), 6.4 (2 H, m), 3.55 (2 H, s), 2.91 (1 H, d, *J* 3.5 Hz), and 1.78 (6 H, s).

(iv) 1-Acetyl-3-methyl-1-phenylindene (50 mg), *N*-phenylmaleimide (346 mg), and diphenyl ether (0.5 ml) were heated at 140 °C (2.5 h). Chromatography of the product on silica in benzene–ether (9 : 1) gave the endo-*adduct* (7; $R^1 = Me$, $R^2 = Ph$, X = COMe) (68 mg, 80%), m.p. 255—258° (from chloroform–ethanol) (Found: C, 79.55; H, 5.4; N, 3.45. $C_{28}H_{23}NO_3$ requires C, 79.8; H, 5.5; N, 3.3%), $\nu_{max.}$ 1 770 and 1 708 cm^{-1}, δ 7.9—7.0 (12 H, m), 6.6—6.3 (2 H, m), 4.09 (1 H, d, *J* 8 Hz), 3.4 (1 H, d, *J* 8 Hz), 3.32 (1 H, s), 1.78 (3 H, s), and 1.45 (3 H, s).

1-Acetyl-1-methyl-3-phenylindene (50 mg), *N*-phenylmaleimide (346 mg), and diphenyl ether were heated at 140 °C (3 h). Isolation as above gave (7; $R^1 = Me$, $R^2 =$ Ph, X = COMe) (65 mg), identical with the previously described sample (mixed m.p. and i.r. spectrum).

(v) 1-Benzoyl-1,3-dimethylindene (62 mg), *N*-phenylmaleimide (173 mg), and diphenyl ether (0.3 ml) were heated at 170 °C (2 h). Chromatography on silica in benzene–ether (9 : 1) gave the endo-*adduct* (70 mg, 67%), m.p. 267—268° (from chloroform–ethanol) (Found: C, 79.8; H, 5.45; N, 3.4. $C_{28}H_{23}NO_3$ requires C, 79.8; H, 5.5; N, 3.3%), $\nu_{max.}$ 1 765, 1 704, and 1 670 cm^{-1}, δ [$(CD_3)_2SO$] 8.2—7.0 (12 H, m, aromatic), 6.6—6.3 (2 H, m, aromatic), 4.43 (1 H, s), 3.72 (2 H, s), and 2.65 (6 H, s).

Cross-over Experiment.—1-Acetyl-1,3-diphenylindene (155 mg, 0.5 mmol), 1-benzoyl-1,3-dimethylindene (124 mg, 0.5 mmol), and diphenyl ether (5 ml) were heated at 150 °C in a sealed tube (Carius oven). The n.m.r. spectrum and t.l.c. of the product showed the presence of only 2-acetyl-1,3-diphenylindene and 2-benzoyl-1,3-dimethylindene.

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[17] K. Hafner and W. Bauer, *Angew. Chem. Internat. Edn.*, **1968**, **7**, 297.