

## Some Derivatives of Indan-1-one. Part II.<sup>1</sup>

By **W. Kemp** \* and **J. Spanswick**, Chemistry Department, Heriot-Watt University, Chambers Street, Edinburgh EH1 1HX

A series of 3-substituted indan-1-ones has been prepared, and the structures of these compounds have been unequivocally established. Bimolecular reduction of these ketones, followed by dehydration, gave either bi-indenyl or *trans*-indanylideneindene derivatives. The mechanisms of these reactions are discussed.

RECENTLY Chio Jen *et al.*<sup>2</sup> claimed to have prepared 3,7-dimethylindan-1-one (I) by the action of crotonic acid on toluene in the presence of polyphosphoric acid. This would involve initial acylation of the toluene nucleus in the 2-position, followed by alkylation in the 3-position, as shown in route (A) (or, less likely, 3-alkylation followed by 2-acylation). As part of our study of bi-indenyl derivatives, we repeated this reaction, and obtained the same product as Chio Jen, but i.r. and n.m.r. spectra indicated that it was 3,5-dimethylindan-1-one (II), formed by initial acylation of the toluene nucleus in the 4-position, followed by alkylation in the 3-position, as shown in route (B) (again, alkylation followed by acylation is possible, but less likely). In

order to verify the structure of the product, we prepared the corresponding alcohol, 3,5-dimethylindan-1-ol, which was subsequently dehydrated to 1,6-dimethylindene. A notable feature in the n.m.r. spectrum of the ketone (II) is the low-field position of the 7-proton signal ( $\tau$  2.25); this appears as the low-field doublet of a pseudo-AB system,  $J_{6,7}$  8,  $J_{4,7}$  0 Hz. This situation could not arise in 3,7-dimethylindan-1-one (I). In the spectrum of the derived alcohol, the low-field doublet appears again, but at  $\tau$  2.90 ( $J_{6,7}$  8 Hz). Dehydration of the alcohol gives the indene in which the 3-proton signal shows long-range coupling ( $J$  0.5 Hz) with the 7-proton.<sup>3</sup>

Both *m*-xylene and *p*-xylene were treated with

<sup>1</sup> F. Bell and J. Spanswick, *J. Chem. Soc. (C)*, 1966, 1887 is to be regarded as Part I.

<sup>2</sup> Chio Jen, Lin-Lin K'uang, Ying-Chun Lin, Chin-Shih Ma, and Seng Chin, *K'o Hsueh T'ung Pao*, 1966, **17** (9), 412 (*Chem. Abs.* 1967, **66**, 3578).

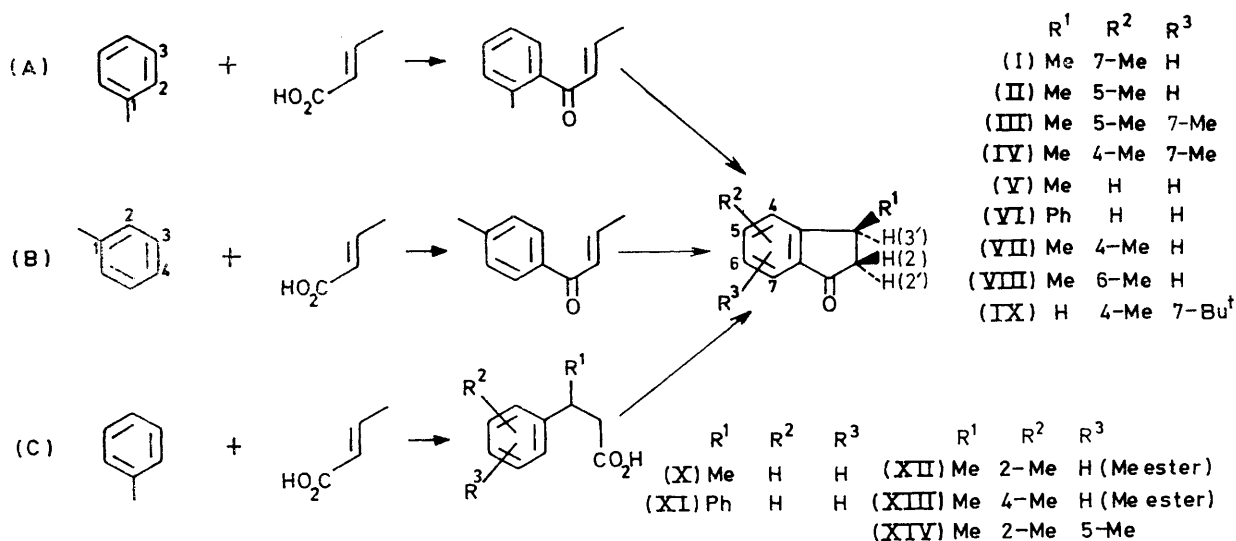
<sup>3</sup> J. A. Elvidge and R. G. Foster, *J. Chem. Soc.*, 1963, 590.

crotonic acid in the presence of polyphosphoric acid, yielding respectively 3,5,7-trimethylindan-1-one (III) and 3,4,7-trimethylindan-1-one (IV) in high yield. As before, the reaction presumably proceeds by initial acylation followed by alkylation.

The reaction between crotonic acid and benzene in the presence of excess of aluminium chloride yielded two products: 3-phenylbutyric acid (X) and 3-methylindan-1-one (V); with cinnamic acid and benzene, the products were 3,3-diphenylpropionic acid (XI) and 3-phenylindan-1-one (VI). The isolation of compounds (X) and (XI) from these reactions indicates that alkylation is the first

chloride-catalysed reaction between crotonic acid and toluene.)

The 3-substituted indan-1-ones were converted into the diols (XXVII) by bimolecular reduction on aluminium amalgam. Dehydration of these diols gave, not the expected 3,3'-bi-indenyls [*e.g.* (XXV)], but the *trans*-1-(indan-1-ylidene)indenenes (XV)–(XIX). The mechanism of these dehydrations is interpreted as shown in Scheme 2. Loss of one molecule of water leads to compounds (XXVIII); thereafter, protonation and loss of water leads to the carbonium ions (XX)–(XXII). If these ions lose a proton from position 2', a bi-indenyl



SCHEME 1

step in the condensation, and is followed by acylation to give the indanones [route (C)]. Further substantiation of this route was obtained from investigation of the action of crotonic acid on toluene (in the presence of an excess of aluminium chloride), which gave two acids and two indanones. The acids were converted into their methyl esters and separated by preparative g.l.c.; the more volatile ester was shown to be methyl 3-(*o*-tolyl)-butyrate (XII) and the other methyl 3-(*p*-tolyl)butyrate (XIII). The two indanones were similarly separated and shown to be 3,4-dimethylindan-1-one (VII) and 3,6-dimethylindan-1-one (VIII). Treatment of each ester with polyphosphoric acid gave the corresponding indan-1-one,<sup>4</sup> and the ease with which these cyclisations occur leads us to conclude that the direct formation of indan-1-ones from crotonic acid and toluene in the presence of excess of aluminium chloride proceeds by initial alkylation followed by acylation. (Chio Jen prepared propenyl *p*-tolyl ketone by the action of crotonyl chloride on toluene in the presence of aluminium chloride. We therefore conclude that no crotonyl chloride is formed as an intermediate in the aluminium

results. Loss of a proton from the 3-position leads to an indanylideneindene.

Diols unsubstituted in the 3-position are dehydrated in high yields to give bi-indenyls, presumably because they are thermodynamically favoured over the corresponding indanylideneindenenes. This hypothesis is supported by the dehydration of 1-(indan-1-yl)indan-1-ol (XXIX) to 3,3'-bi-indenyl<sup>5</sup> with production of less than 1% of 1-(indan-1-ylidene)indene. The carbonium ion (XXX) probably undergoes a 1,3-hydrogen migration to yield an ion of the type (XX), with deprotonation proceeding to yield a bi-indenyl. An alkyl or an aryl substituent in the 3-position reduces the C(3)–H bond dissociation energy, and in consequence favours the formation of indanylideneindenenes.

Marechal and Sigwalt<sup>5</sup> have shown that the yellow colour associated with 3,3'-bi-indenyl is due to contamination by indanylideneindene. Bell and Waring<sup>6</sup> have reported that dehydration of the diol formed from 4,7-dimethylindan-1-one yields a colourless bi-indenyl, indicating the absence of a derivative of indanylideneindene. We have found that dehydration of the diol from 3,4,7-trimethylindan-1-one leads to a bi-indenyl

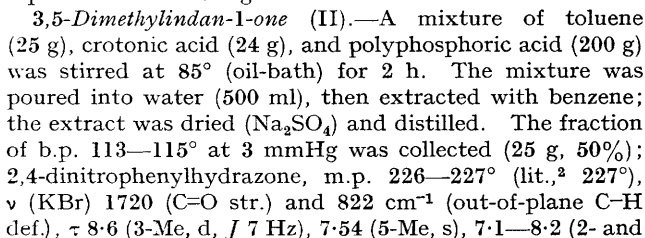
<sup>4</sup> P. T. Lansbury and N. R. Mancuso, *J. Amer. Chem. Soc.*, 1966, **88**, 1205.

<sup>5</sup> E. Marechal and P. Sigwalt, *Bull. Soc. chim. France*, 1966, 1075.

<sup>6</sup> Y. Altman and D. Ginsberg, *J. Chem. Soc.*, 1961, 1498; F. Bell and D. H. Waring, *ibid.*, 1949, 2689.



trans-1-(3,5-Dimethylindan-1-ylidene)-3,5-dimethylindene (XV).—A solution of 3,5-dimethylindan-1-one (30 g) in benzene (150 ml) and ethanol (250 ml) was reduced with amalgamated aluminium during 12 h. The mixture was



poured into dilute hydrochloric acid and the acid layer was washed with benzene. The combined organic liquors were washed with water, dried ( $\text{Na}_2\text{SO}_4$ ), and concentrated. The mixture of oily diols was dehydrated by refluxing with glacial acetic acid (100 ml) for 2 h. On cooling, a yellow solid was deposited, which was recrystallised from petroleum (b.p. 60–80°) and then from ethanol to give *needles* (5 g, 19%), m.p. 169–171° (Found: C, 92.2; H, 7.75.  $\text{C}_{22}\text{H}_{22}$  requires C, 92.3; H, 7.7%).  $\nu_{\text{max}}$  (KBr) 808  $\text{cm}^{-1}$ ,  $\lambda_{\text{max}}$  (EtOH) 208, 247, 294, 346sh, 362, and 373sh nm (log  $\epsilon$  4.35, 4.07, 4.18, 4.34, 4.47, and 4.41),  $\tau$  8.6 (3'-Me, d,  $J_{3,3'}$  6.5 Hz), 7.72br (3-Me, s), 7.61 (5'-Me, s), 7.57 (5-Me, s), 6.0–7.25 (2'- and 3'-H, m), 2.95 (2-H, signal almost masked by those of aromatic protons), 2.67–2.9 (4-, 4', 6-, and 6'-H, m), 2.35 (7-H), d,  $J_{6,7}$  8 Hz), and 2.1 (7'-H, d,  $J_{6,7'}$  8 Hz). The bulk of the product, obtained by diluting the glacial acetic acid solution, was a dark red glassy solid which did not undergo any Diels-Alder reactions.

**3-Methylindan-1-one (V).**—This compound had b.p. 103° at 3 mmHg (lit.,<sup>3</sup> 132–137° at 15 mmHg and 118–119° at 11 mmHg),  $\nu_{\text{max}}$  (KBr) 1708  $\text{cm}^{-1}$  (C=O str.),  $\tau$  8.37 (3-Me, d), 7.9 (2'-H, q), 7.23 (2-H, q), 6.7 (3'-H, decet) ( $J_{3,3'}$  8,  $J_{2,3'}$  8,  $J_{2,3}$  5,  $J_{2,2'}$  19 Hz), and 2.3–2.9 (aromatic protons).

**trans-3-Methyl-1-(3-methylindan-1-ylidene)indene (XVI).**—3-Methylindan-1-one (24 g) was reduced (as before) to a mixture of diols, which were dehydrated by refluxing in benzene containing a few crystals of toluene-4-sulphonic acid. The crude diene was recrystallised from isopropyl alcohol to give an orange *solid*, which was further recrystallised from methanol; yield 5 g, m.p. 102–103° (Found: C, 92.3; H, 7.3.  $\text{C}_{20}\text{H}_{18}$  requires C, 93.0; H, 7.0%).  $\nu_{\text{max}}$  (KBr) 755  $\text{cm}^{-1}$ ,  $\lambda_{\text{max}}$  (EtOH) 208, 228sh, 239, 291, 325sh, 342, 351, and 358 nm (log  $\epsilon$  4.13, 4.01, 4.03, 4.08, 4.05, 4.26, 4.32, and 4.27),  $\tau$  8.64 (3-Me, d,  $J_{3,3'}$  7 Hz), 7.75 (3-Me, t), 6.1–7.35 (2'- and 3'-H, m), 2.9 (2-H, t,  $J_{2,3}$  1.2 Hz), 2.56–2.83 (4-, 4', 5-, 5', 6-, and 6'-H, m), 2.23–2.5 (7-H, m), and 1.93–2.21 (7'-H, m).

**3-Phenylindan-1-one<sup>3</sup> (VI).**—This material showed  $\tau$  7.52 (2-H, q), 6.95 (2'-H, q), 5.54 (3'-H, q) ( $J_{2,2'}$  19,  $J_{2,3'}$  8,  $J_{2,3}$  5 Hz), 2.45–3.1 (8 aromatic protons), and 2.32 (7-H, m).

**3-Phenyl-1-(3-phenylindan-1-ylidene)indene (XVII).**—3-Phenylindan-1-one (35 g) was submitted to bimolecular reduction then dehydration as before; the crude diene was recrystallised from petroleum (b.p. 60–80°) to yield an orange *solid* (3.7 g), m.p. 181–183° (Found: C, 93.5; H, 6.0.  $\text{C}_{30}\text{H}_{22}$  requires C, 94.2; H, 5.8%).  $\nu_{\text{max}}$  (KBr) 700, 740, and 750  $\text{cm}^{-1}$ ,  $\lambda_{\text{max}}$  (hexane) 244, 257, 299, 340sh, 357, and 364 nm (log  $\epsilon$  4.48, 4.47, 4.19, 4.35, 4.55, and 4.49),  $\tau$  6.55 (2-H, q), 5.92 (2'-H, q), 5.55 (3'-H, q) ( $J_{2,2'}$  17,  $J_{3,2'}$  8,  $J_{3,2}$  5 Hz), 2.45–3.1 (17H), 2.25 (7-H, m), and 1.9 (7'-H, m).

**Condensation of Crotonic Acid with Toluene in the Presence of Aluminium Chloride.**—A solution of crotonic acid (68 g) in toluene (500 ml) was added to powdered aluminium chloride (318 g) and the mixture was warmed on a water-bath for 5 h. The resulting red solution was poured into ice-hydrochloric acid and extracted with benzene. The combined extracts were washed with water, sodium hydroxide solution, and water, then dried ( $\text{Na}_2\text{SO}_4$ ) and concentrated. The residue was distilled under reduced pressure to yield material (98 g), b.p. 118–120° at 3 mmHg

(66% conversion of crotonic acid into crude ketones). The sodium hydroxide extract was acidified with hydrochloric acid, and the precipitated oil was extracted into benzene; the solution was washed, dried, and distilled to yield mixed acids (40 g), b.p. 160–162° at 2 mmHg. These were converted into their methyl esters, b.p. 82–86° at 1.5 mmHg, and separated by preparative g.l.c. The more volatile was methyl 3-(*o*-tolyl)butyrate (XII),  $\nu_{\text{max}}$  (film) 1735, 785, 763, and 700  $\text{cm}^{-1}$ ,  $\tau$  2.87 (4H, s, aromatic), 6.47 (Me of ester, s), 6.76 ( $\beta$ -H, qt), 7.58 ( $\alpha$ -H, d,  $J_{\alpha\beta}$  2 Hz), 8.72 ( $\gamma$ -H, d,  $J_{\beta\gamma}$  8 Hz), and 7.46 (aryl Me, s).

The less volatile ester was methyl 3-(*p*-tolyl)butyrate (XIII),  $\nu_{\text{max}}$  (film) 1735, 815, 762, and 700  $\text{cm}^{-1}$ ,  $\tau$  2.96 and 3.01 (4H, aromatic, approximate  $A_2B_2$  system), 6.47 (Me of ester, s), 6.76 ( $\beta$ -H, qt), 7.57 ( $\alpha$ -H, d,  $J_{\alpha\beta}$  2 Hz), 8.75 ( $\gamma$ -H, d,  $J_{\beta\gamma}$  8 Hz), and 7.68 (aryl Me, s).

The indan-1-ones were similarly separated by preparative g.l.c. to give 3,4-dimethylindan-1-one (VII) as the most volatile ketone,  $\nu_{\text{max}}$  (KBr) 1700 and 790  $\text{cm}^{-1}$ ,  $\tau$  2.4–3.1 (3H, aromatic), 6.7 (3'-H, decet), 7.25 (2-H, q), 7.9 (2'-H, q) ( $J_{3,2}$  8,  $J_{3,2'}$  5,  $J_{2,2'}$  19 Hz), 7.45 (4-Me, s), and 8.64 (3'-Me, d,  $J_{3,3'}$  8 Hz).

The second ketone was 3,6-dimethylindan-1-one (VIII),  $\nu_{\text{max}}$  (KBr) 1700 and 820  $\text{cm}^{-1}$ ,  $\tau$  2.4–3.25 (3H, aromatic), 6.7 (3'-H, decet), 7.2 (2-H, q), 7.9 (2'-H, q) ( $J_{3,2}$  8,  $J_{3,2'}$  5,  $J_{2,2'}$  19 Hz), 7.6 (6-Me, s), and 8.65 (3-Me, d,  $J_{3,3'}$  8 Hz); semicarbazone, m.p. 220° (lit.,<sup>7</sup> 224°); 2,4-dinitrophenylhydrazones, m.p. 195–198° (lit.,<sup>8</sup> 271°),  $\tau$  0.9 (3'-H, d,  $J_{3',5'}$  2.5 Hz), 1.65 (5'-H, q), 1.92 (6'-H, d,  $J_{5',6'}$  9 Hz), 2.34 (7-H, s), 2.72 (4- and 5-H, s), 6.4–7.6 (3', 2', and 2'-H, m), 7.56 (6-Me, s), and 8.57 (3-Me, d,  $J_{3,3'}$  7 Hz).

**3,4,7-Trimethylindan-1-one (IV).**—(a) *Polyphosphoric acid route.* A mixture of *p*-xylene (20 g), crotonic acid (20 g), and polyphosphoric acid (200 g) was stirred at 100° for 2 h, gradually forming a red solution. The mixture was poured into cold water and steam distilled. The steam distillate was extracted with benzene; the benzene solution was dried and evaporated on a steam-bath, and the residue was distilled to give 3,4,7-trimethylindan-1-one (16.5 g), b.p. 100° at 3 mmHg, m.p. 32–33° (lit.,<sup>9</sup> m.p. 32°),  $\tau$  8.76 (3-Me, d), 7.7 (4-Me, s), 7.52 (7-Me, s), 7.86 (2'-H, q), 7.25 (2-H, q), 6.5–6.95 (3'-H, decet) ( $J_{3,3'}$  7.5,  $J_{2,3'}$  7.5,  $J_{2,3}$  2,  $J_{2,2'}$  19 Hz), 2.91 (5-H, d), and 2.69 (6-H, d,  $J_{5,6}$  7.5 Hz).

(b) *Aluminium chloride route.*—A solution of crotonic acid (68 g) in *p*-xylene (500 ml) was added slowly to powdered aluminium chloride (318 g) and the slurry was heated on a water-bath for 5 h with occasional shaking. The mixture was poured into ice-water and the organic material was extracted into benzene. The extract was washed with water and then sodium hydroxide solution [which on acidification yielded 2,5-dimethyl-3-phenylbutyric acid, (XIV) (73 g)]. The remaining benzene layer was washed with water, dried ( $\text{Na}_2\text{SO}_4$ ) and evaporated; the residue was distilled to yield the crude indan-1-one derivative (45 g). The butyric acid derivative was converted into 3,4,7-trimethylindan-1-one by stirring with polyphosphoric acid at 100° for 2 h; yield 55 g after distillation; total yield of (IV) 100 g (58%).

**1,1',4,4',7,7'-Hexamethyl-3,3'-bi-indenyl (XXVI).**—The crude 3,4,7-trimethylindan-1-one (60 g) was reduced with aluminium amalgam (18 g) and the crude diol was dehydrated by refluxing in dry benzene with a few crystals of toluene-4-sulphonic acid. The cooled solution was washed

<sup>7</sup> T. Wagner-Jauregg and H. Hippchen, *Ber.*, 1943, **76B**, 94.

<sup>8</sup> H. Pines, D. R. Strehlau, and V. N. Ipatieff, *J. Amer. Chem. Soc.*, 1949, **71**, 3534.

<sup>9</sup> P. A. Plattner, A. Furst, and H. Schmid, *Helv. Chim. Acta*, 1945, **28**, 1647.

with water, dried, and concentrated, and the residue was dissolved in isopropyl alcohol; cooling yielded a tacky solid. This material was purified by chromatography on alumina; the first fraction was crystallised from ethanol to give the *bi-indenyl* (XXVI), m.p. 126—128° (Found: C, 91.7; H, 8.15.  $C_{24}H_{26}$  requires C, 91.7; H, 8.3%),  $\lambda_{\max}$  (EtOH) 220 and 264 nm (log  $\epsilon$  4.46 and 4.07),  $\tau$  2.09 (4H, s, aromatic), 3.72 (2- and 2'-H, q), 6.43 (3- and 3'-H, octet,  $J_{3,2}$  4 Hz), 8.65 (1-Me, q,  $J_{1,1}$  7,  $J_{1,2}$  1.5 Hz), 7.58 (7- and 7'-Me, s), and 7.9 and 8.0 (4- and 4'-Me). It is not clear from models why the two 4-methyl groups are in different environments.

The second chromatography fraction, on recrystallisation from petroleum (b.p. 60—80°), yielded yellow crystals (0.5 g), m.p. 208°, identified (n.m.r. spectrum) as 3,4,6-trimethyl-1-(3,4,6-trimethylindan-1-ylidene)indene (XIX). This must have originated from the presence of 3,4,6-trimethylindan-1-one as an impurity in the starting materials (Found: C, 92.0; H, 8.2.  $C_{24}H_{26}$  requires C, 91.7; H, 8.3%),  $\nu_{\max}$  (KBr) 866 and 800  $\text{cm}^{-1}$ ,  $\lambda_{\max}$  (EtOH) 210, 250, 290, 293, 365, and 378 nm (log  $\epsilon$  4.25, 4.04, 4.07, 4.10, 4.36, and 4.33),  $\tau$  2.26 (7'-H, s), 2.55 (7-H, s), 2.91 (5- and 5'-H, s), 2.95 (2-H, q,  $J_{2,3}$  1 Hz), 6.0—7.3 (2'- and 3'-H, m), 7.5—7.8 (3-, 4-, 4'-, 6-, and 6'-Me, m), and 8.62 (3'-Me, d,  $J_{3',Me}$  6.5 Hz).

**3,5,7-Trimethylindan-1-one (III).**—A mixture of *m*-xylene (32 g) and crotonic acid (27 g) was stirred at 100° for 2 h with polyphosphoric acid (200 g). Isolation as before yielded the *ketone* (III) (40 g), b.p. 120° at 1 mmHg, m.p. 36—38° [from petroleum (b.p. 60—80°)] (Found: C, 82.6; H, 7.9.  $C_{12}H_{14}O$  requires C, 82.8; H, 8.0%),  $\nu_{\max}$  (KBr) 1700 and 855  $\text{cm}^{-1}$ ,  $\tau$  3.0 (6-H, s), 3.2 (4-H, s), 6.85 (3'-H, decet), 7.3 (2-H, q), 7.72 (2'-H, q,  $J_{3',2}$  7,  $J_{3',2'}$  4,  $J_{2',2}$  19 Hz), 7.6 (7-Me, s), 7.7 (5-Me, s), and 8.7 (3-Me, d,  $J_{3,Me}$  7 Hz).

**4-Methyl-7-*t*-butylindan-1-one (IX).**—4-*t*-Butyltoluene

was chloromethylated<sup>10</sup> to yield 5-*t*-butyl-2-methylbenzyl chloride, b.p. 112—115° at 12 mmHg (lit.,<sup>5</sup> 146—147° at 26 mmHg), and 2,6-bis(chloromethyl)-4-*t*-butyltoluene (XXIII), b.p. 152—158° at 12 mmHg, m.p. 77—78° [from petroleum (b.p. 60—80°)] (Found: C, 64.0; H, 7.2.  $C_{13}H_{18}Cl_2$  requires C, 63.7; H, 7.3%).

Diethyl 2-methyl-5-*t*-butylbenzylmalonate was prepared from the corresponding benzyl chloride; hydrolysis and decarboxylation gave the crude acid. The acid was cyclised with polyphosphoric acid (2 h at 100°) to yield 4-methyl-7-*t*-butylindan-1-one, m.p. 81° (Found: C, 82.5; H, 8.8.  $C_{14}H_{18}O$  requires C, 83.1; H, 8.9%),  $\nu_{\max}$  (KBr) 1700  $\text{cm}^{-1}$ ,  $\tau$  8.55 (7-Bu<sup>t</sup>, s), 7.7 (4-Me, s), 7.2—7.5 (2  $\times$  3-H, m), 6.85—7.15 (2-H, m), and 2.69 (5- and 6-H, s); *oxime*, m.p. 181—185° (Found: C, 77.3; H, 8.4.  $C_{14}H_{19}NO$  requires C, 77.4; H, 8.7%),  $\tau$  8.52 (7-Bu<sup>t</sup>, s), 7.75 (4-Me, s), 7.3 (2- and 3-H, s), 2.9 (5-H, d), 2.7 (6-H, d,  $J_{5,6}$  8 Hz), and 2.57 (OH, s); 2,4-dinitrophenylhydrazone, m.p. 268° (decomp.) (Found: C, 62.6; H, 6.0.  $C_{20}H_{22}N_4O_4$  requires C, 62.8; H, 5.8%).

**4-Methyl-8-*t*-butyl-5-hydrindacene-1,7-dione (XXIV).**—2,6-Dichloromethyl-4-*t*-butyltoluene (XXIII) was subjected to the same series of reactions as 2-methyl-5-*t*-butyltoluene; polyphosphoric acid ring closure of 4-*t*-butyltoluene-2,6-dipropionic acid gave the *diketone* (XXIV) in low yield, m.p. 152—155° (Found: C, 79.2; H, 7.7.  $C_{17}H_{20}O_2$  requires C, 79.7; H, 7.8%),  $\nu_{\max}$  (KBr) 1710  $\text{cm}^{-1}$ ,  $\tau$  8.52 (8-Bu<sup>t</sup>, s), 7.8 (4-Me, s), 7.25—7.55 (3- and 5-H, m), and 6.9—7.17 (2- and 6-H, m).

We thank the S.R.C. for a grant (to J. S.).

[1/1074 Received, June 28th, 1971]

<sup>10</sup> R. Berg, *Roczniki Chem.*, 1934, **14**, 1249.