121. *Synthesis of Cyclic Hydrocarbons. Part IV.* Alkylindanes.*

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Syntheses of fourteen alkylindanes, by methods which exclude simultaneous formation of isomers, are described.

Although many simple alkylindanes have been described, the methods generally used for their preparation have not necessarily led to the pure hydrocarbons, so the physical properties recorded are often of questionable accuracy. The infrared and ultraviolet spectra of alkylindanes had also been neglected until recently, when the spectra and physical properties of the monomethyl- and several dimethyl-indanes were published;[1] the purity of these compounds was stated to be not less than 95%.

The shortest direct route to the required alkylindanes has been used, namely, the synthesis of the alkyl-β-phenyl-propionic acid or -butyric acid and its cyclisation to the alkylindanone. Care has been taken to avoid isomerisation and to determine optimum conditions for each reaction. The general route is indicated in the annexed scheme (R = H or Me).

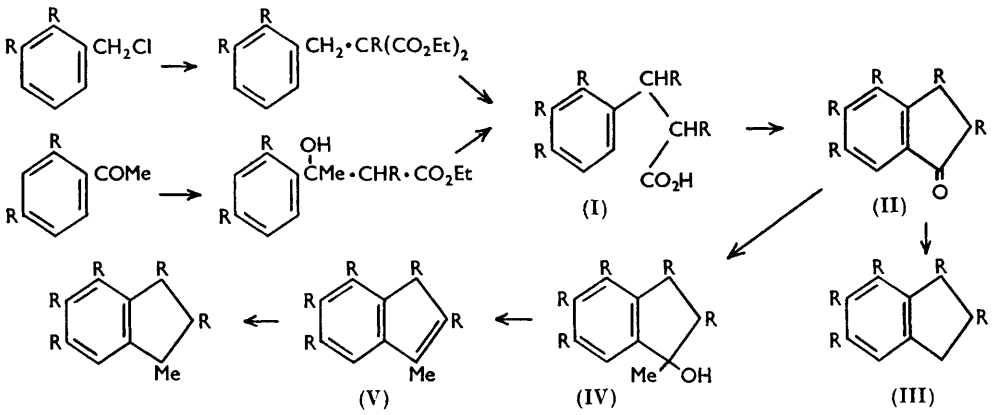
The acids (I) are generally high-melting and readily purified by crystallisation. The

* Part III, preceding paper.

[1] Entel, Ruof, and Howard, *Analyt. Chem.*, 1953, **25**, 1303; Entel, *ibid.*, 1954, **26**, 612.

*iso*butyric esters were prepared by the malonic ester synthesis, and the *iso*valeric esters by a Reformatsky reaction.

Diethyl 2-methylbenzyl- and diethyl methyl-2-methylbenzyl-malonate were preferably hydrolysed in two stages as hydrolysis of the second ester group was much slower than that of the first.[2] On the other hand, both ester groups of diethyl 2 : 3-dimethylbenzyl- and methyl-(2 : 3-dimethylbenzyl)-malonate were readily hydrolysed.



α-Methyl-β-*o*-tolylpropionic acid was exceptional in that it was liquid,[3] even after repeated crystallisation of the *p*-nitrobenzyl ester and regeneration of the acid by catalytic hydrogenolysis.

In an attempt to prepare α-methyl-β-*o*-tolylbutyric acid, when 2-methylacetophenone was used in the Reformatsky reaction with ethyl α-bromopropionate (under the conditions used in the analogous reaction of 4-methylacetophenone), ethyl 2-methyl-3-*o*-tolylbut-2-enoate was obtained in low yield, most of the 2-methylacetophenone being recovered. The temperature (100°) at which the reaction was conducted was higher than is reported by Ruzicka and Ehmann [4] to cause condensation in good yield; zinc dust, zinc foil, and a highly active zinc–copper couple [5] gave the same result. As the bromozinc ester was formed smoothly, the failure of the reaction was possibly due to steric hindrance of the carbonyl group of the ketone by the *o*-methyl group.[6] Uncontrollable reaction of 2-methylacetophenone, ethyl bromoacetate, and zinc started when the addition of reactants was almost complete, and caused loss of all material : the reaction was not investigated further.

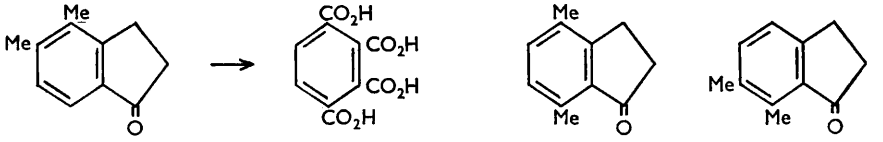
Attempts to cyclise β-*o*-tolylpropionic acid with sulphuric acid,[7] toluene-*p*-sulphonic acid, or boron trifluoride failed. Stannic chloride [8] had no effect on β-*p*-tolylbutyryl chloride in solution in light petroleum at room temperature. Anhydrous aluminium chloride may cause isomerisation [9] and so is unsuitable : so is polyphosphoric acid [10] since it causes self-condensation of the resulting indanone, and may also promote isomerisation.[11] However, in the presence of anhydrous hydrogen fluoride, the *iso*butyric acids underwent ring-closure quantitatively, the only losses occurring during isolation and purification. It was necessary to exclude atmospheric moisture since the reaction, unless it is very rapid, stops when the hydrogen fluoride has absorbed sufficient moisture, and cyclisation is then

[2] Cf. Pfau and Plattner, *Helv. Chim. Acta*, 1939, **22**, 202.
[3] Fusco and Rossi, *Gazzetta*, 1948, **78**, 524.
[4] Ruzicka and Ehmann, *Helv. Chim. Acta*, 1932, **15**, 140.
[5] Howard, *J. Res. Nat. Bur. Stand.*, 1940, **24**, 677.
[6] Cf. Dippy and Parkins, *J.*, 1951, 1570.
[7] Bachmann and Raunio, *J. Amer. Chem. Soc.*, 1950, **72**, 2530.
[8] Pines, Strehlau, and Ipatieff, *ibid.*, 1949, **71**, 3534.
[9] Baddeley, Holt, and Makar, *J.*, 1952, 3289; Colonge and Weinstein, *Bull. Soc. chim. France*, 1951, 961.
[10] Snyder and Werber, *J. Amer. Chem. Soc.*, 1950, **72**, 2965.
[11] Mosby, *J. Org. Chem.*, 1953, **18**, 485.

incomplete. The product was pure except for a trace of yellow polymer which remained as a residue when the product was distilled in steam.

Anhydrous hydrogen fluoride is the only known catalyst for this reaction which combines the necessary activity with a freedom from undesirable side-reactions such as self-condensation, rearrangement, or substitution. It does not cause migration of substituents in aromatic compounds at room temperature,[12] except by intramolecular displacement of an alkyl group by an acylonium ion which takes place only if the alternative cyclisation, with displacement of a proton, is not possible.[13]

The orientation of 4 : 5-dimethylindanone was proved by oxidising it to mellophanic acid (VI). Although either of the structures (VII) or (VIII) would have given mellophanic



(VI) (VII) (VIII)

acid on oxidation, these were excluded because the former represents the known 4 : 7-dimethylindanone [14] and they would have been expected to show diminished reactivity towards semicarbazide and hydroxylamine, owing to steric hindrance of the carbonyl group by the 7-methyl group, as has been observed with 3 : 4 : 7-trimethylindanone.

As an alternative route to alkylindanones, the reaction of *p*-xylene with crotonic acid in the presence of anhydrous hydrogen fluoride at room temperature was investigated. Hydrogen fluoride has been used at 80° under pressure as a catalyst for this type of reaction by Hart and Tebbe.[14] As hydrogen fluoride has been observed to promote the transfer of the methyl group from xylene to benzene at higher temperatures,[15] it is desirable that the reaction be conducted at room temperature. It was found that, although *p*-xylene is soluble in anhydrous hydrogen fluoride in the presence of a molar proportion of crotonic acid, it soon separated from solution. The apparatus was unsuitable for the vigorous long agitation and reaction was thereby limited to the interface of the two phases: consequently, after 96 hr. the yield of 3 : 4 : 7-trimethylindanone was only 14%.

The alkylindanones were reduced to the corresponding alkylindanes (III) by the Clemmensen method. Traces of the alkylindene were also formed,[16] but were removed when the product was heated with potassium. The Huang-Minlon modification of the Wolff–Kishner reaction is unsuitable for the reduction of indanones.

The alkylindanones with methylmagnesium iodide gave the corresponding alkyl-1-methylindanol (IV), although the use of the more reactive alkyl-lithium is preferable for the introduction of alkyl groups other than methyl. Indanones unsubstituted in position 2 also give a solid by-product during this reaction, which probably results from self-condensation at position 2, since 2-substituted indan-1-ones, in which the position is blocked, give the normal product in high yield. To reduce the extent of this side-reaction, the concentration of the alkylindanone is kept as low as possible during the Grignard reaction. The side-reaction is even more pronounced with the less stable indan-2-one,[17] so that reaction with hexylmagnesium bromide gave none of the required product.

The alkyl-1-methylindanols were too unstable to be isolated in the pure state,[18] which obviated the need for a vigorous dehydrating agent which usually causes some polymerisation of the product.[19] The alkyl-1-methylindanol underwent quantitative conversion

[12] Calcott, Tinker, and Weinmayr, *J. Amer. Chem. Soc.*, 1939, **61**, 1010.
[13] Badger, Caruthers, and Cook, *J.*, 1949, 2044; Aitken, Badger, and Cook, *J.*, 1950, 331.
[14] Hart and Tebbe, *J. Amer. Chem. Soc.*, 1950, **72**, 3286.
[15] Lee and Radford, U.S.P. 2,416,184.
[16] Levy, *Ann. Chim.*, 1938, **9**, 5.
[17] Plattner and Fürst, *Helv. Chim. Acta*, 1945, **28**, 1636.
[18] Cf. von Braun and Kirschbaum, *Ber.*, 1913, **46**, 3046.
[19] Jamison, Lesslie, and Turner, *J. Inst. Petroleum*, 1949, **35**, 615.

into the corresponding alkylindene (V), without any appreciable polymerisation, when heated in benzene with a small amount of dilute aqueous sulphuric acid. Under these conditions the position of the double bond of the alkylindene is fixed.[20]

1 : 2 : 4-Trimethyl- and 1 : 2 : 4 : 5-tetramethyl-indene were the only two hydrocarbons prepared in this investigation which formed picrates sufficiently stable for isolation. The picrate of the former could not be recrystallised, as it was partly dissociated in solution and only the less soluble component crystallised; the picrate of the latter was stable. The picrates of the corresponding indanes could not be isolated.

Unless the alkylindene could be purified by crystallisation, the product was converted directly into the alkylindane by catalytic hydrogenation, since the alkylindenes are insufficiently stable to be fractionally distilled, even in the presence of polymerisation-inhibitors, while oxygenated impurities could not be removed by the usual methods. The alkylindanes were purified by heating them with potassium at 145° for two hours, before being fractionally distilled.

Several of the methylindanes described here can have geometrically isomeric forms, although no alkylindane has previously been reported to have been obtained as the pure stereoisomer. By analogy with the dimethyl*cyclo*pentanes, the isomers should differ slightly in physical properties, but it is uncertain as to whether the difference in boiling point is sufficient to have permitted the complete separation of the *cis*- and *trans*-isomers of 1 : 2 : 5- and 1 : 3 : 5-trimethylindane, and of the *cis-cis*- and *cis-trans*-isomers of 1 : 2 : 3 : 5-tetramethylindane.

Hydrogenation of a double bond in the presence of palladium under mild conditions has been shown to result almost exclusively in *cis*-addition,[21] and selective catalytic hydrogenation of disubstituted acetylenes produces exclusively the *cis*-olefins.[22] Consequently, it may be inferred that 1 : 2 : 4-trimethyl- and 1 : 2 : 4 : 5-tetramethylindane, prepared by the catalytic hydrogenation of the corresponding indene at room temperature, have been obtained as the *cis*-isomer. Determinations of purity by vapour-phase partition chromatography have shown these two compounds to be pure.

Infrared Spectra.—The infrared spectra of 4-methyl-, 2 : 4- and 4 : 5-dimethyl- and 2 : 4 : 5- and 3 : 4 : 7-trimethyl-indanone, and of 1 : 2 : 4- and 1 : 4 : 5-trimethyl- and 1 : 2 : 4 : 5-tetramethyl-indene were determined for comparison with those of the alkylindanes.

The carbonyl absorption maxima of the methylindanones (5·88 $\pm$ 0·02 μ) accord with the usual finding that in five-membered ring ketones the characteristic band wavelength has decreased as a result of ring strain. This effect is apparent, despite the expected bathochromic shift in wavelength due to $\alpha\beta$-unsaturation.

The methylindenes show absorption maxima at approximately 6·1 and 6·3 μ, corresponding to the stretching frequency of a conjugated double bond. A band also appears at approximately 7·18 μ, which, although outside the double-bond stretching frequency, is absent from the spectra of all the alkylindanes studied and may therefore be characteristic of the indene nucleus.

Isomeric alkylindanes are readily identified. The spectra of all the compounds studied showed absorption bands corresponding to the out-of-plane vibrations of the hydrogen atoms of the aromatic ring. These bands are characteristic of the positions of substitution of the aromatic ring, as found in the benzene series. These bands are found for indanes: unsubstituted in the aromatic ring at 13·3—13·5 μ; 4-substituted at 12·9—13·1 μ; 5-substituted at 12·3—12·38 μ; and 4 : 5-substituted at 12·2—12·5 μ. The bands appearing in the overtone regions between 5 and 6 μ are also characteristic of each group and are suitable for the determination of the position of substituents in the aromatic ring.

Determination of Purity.—The authors are indebted to Messrs. C. S. G. Phillips and

[20] Koelsh and Scheiderbauer, *J. Amer. Chem. Soc.*, 1943, **65**, 2311.
[21] Linstead and his collaborators, *ibid.*, 1942, **64**, 1985 *et seq.*
[22] Elsner and Paul, *J.*, 1953, 3156.

I. W. Scott for the determination of the purities of these alkylindanes by gas–liquid partition chromatography (cf. Part II).

Of the fourteen indanes investigated eight gave single peaks, indicating a purity of at least 99%. The other six appeared to decompose on the column, giving a quantity of very low-boiling material and two separate peaks. The following experiments have been carried out to investigate this decomposition.

(1) The material represented by the first peak of the 1 : 3 : 5-trimethylindane was collected and re-injected into the apparatus. It emerged unchanged. (2) The material of both peaks was collected separately and tested for unsaturation. Only the material of the smaller, second peak proved to be unsaturated. (3) 1 : 2 : 4- and 1 : 4 : 5-Trimethyl- and 1 : 2 : 4 : 5-tetramethyl-indene gave no peak due to very low-boiling material, and one single peak which corresponded to the smaller unsaturated peak produced by the corresponding indane. This suggests that some of the indanes decompose into the corresponding indenes and a stable saturated compound.

Isomeric indanes, other than stereoisomers, were completely separated, giving discrete peaks obtained from the pure compound. This indicates that the indanes are free from structural isomers.

Some properties are reported in the annexed Table. A full report on the purity of the alkylindanes described in this paper, as determined by vapour-phase chromatography, and of their infrared and ultraviolet spectra and other physical properties will be published elsewhere.

Indane	B. p./mm.	d^{20}	n_D^{20}	n_D^{25}
4-Me	85·4°/15	0·9577	1·5356	1·5333
1 : 4-Me_2	88·8/13	0·9515	1·5265	1·5245
1 : 5-Me_2	89·6/13	0·9370	1·5222	1·5202
2 : 4-Me_2	92·8/14	0·9314	1·5219	1·5197
4 : 5-Me_2	103·7/14	0·9648	1·5393	1·5373
cis-1 : 2 : 4-Me_3	95·6/11	0·9333	1·5201	1·5181
1 : 2 : 5-Me_3	94·2/12	0·9136	1·5128	1·5108
1 : 3 : 5-Me_3	97·1/14	0·9233	1·5160	1·5138
1 : 4 : 5-Me_3	115·8/15	0·9393	1·5288	1·5268
2 : 4 : 5-Me_3	109·4/12	0·9361	1·5262	1·5240
1 : 2 : 3 : 5-Me_4	109·8/12	0·9305	1·5193	1·5173
cis-1 : 2 : 4 : 5-Me_4	118·9/14	0·9437	1·5254	1·5234
1-Bu	113·2/9	0·9226	1·5137	1·5117
1-Hexyl	143·8/11	0·9091	1·5070	1·5052

Experimental

Substituted β-Phenylpropionic Acids.—The substituted benzyl chloride [23] (1 mole) was allowed to react with a suspension of diethyl sodiomalonate (1 mole) or methylsodiomalonate (1 mole) in boiling benzene (1 l.). When the reaction was complete (8 hr.), the mixture was washed with water containing a trace of hydrochloric acid, and again with water, and the benzene solution was fractionally distilled. The following were prepared : diethyl 2-methylbenzylmalonate (207·8 g., 78·7%), b. p. 133°/0·2 mm., n_D^{15} 1·4940 (Found : C, 68·1; H, 7·4. Calc. for $C_{15}H_{20}O_4$: C, 68·2; H, 7·6%) (Hoch [24] gives b. p. 180—182°/15 mm.); diethyl methyl-2-methylbenzylmalonate (240·7 g., 86·6%), b. p. 105—106°/0·08 mm., n_D^{18} 1·4919 (Found : C, 69·3; H, 8·1. Calc. for $C_{16}H_{22}O_4$: C, 69·1; H, 8·0%) (Bachmann *et al.*[25] give b. p. 184—190°/21 mm.); *diethyl* 2 : 3-*dimethylbenzylmalonate* (244 g., 87·5%), m. p. 41·5—42·5°, b. p. 122°/0·05 mm. (Found : C, 69·2; H, 8·0. $C_{16}H_{22}O_4$ requires C, 69·1; H, 8·0%); *diethyl* (2 : 3-*dimethylbenzyl*)*methylmalonate* (274 g., 94%), b. p. 126°/0·15 mm., n_D^{19} 1·4960 (Found : C, 69·6; H, 8·1. $C_{17}H_{24}O_4$ requires C, 69·8; H, 8·3%).

The malonic ester was heated with an excess of potassium hydroxide in 75% aqueous ethanol for 2 hr. The ethanol was allowed to distil off, and the ice-cold solution was made strongly acid with hydrochloric acid. The malonic esters derived from 2-methylbenzyl chloride gave predominantly the corresponding half-ester, whereas those derived from 2 : 3-dimethylbenzyl chloride gave the pure malonic acid. The product was decarboxylated to give either an

[23] Smith and Spillane, *J. Amer. Chem. Soc.*, 1940, **62**, 2639.
[24] Hoch, *Compt. rend.*, 1931, **192**, 1464.
[25] Bachmann, Cook, Hewett, and Iball, *J.*, 1936, 54.

ester, which was then hydrolysed to the acid, or an acid. The following were thus obtained: β-2-methylphenylpropionic acid (82·2 g., 63·9%), m. p. 103—104° (Found: C, 73·0; H, 7·6. Calc. for $C_{10}H_{12}O_2$: C, 73·1; H, 7·4%) (lit.,[26] m. p. 102—103°) [p-*bromophenacyl ester*, m. p. 74—74·5° (Found: C, 59·7; H, 4·7; Br, 22·1. $C_{18}H_{17}O_3Br$ requires C, 59·9; H, 4·7; Br, 22·1%)]; α-methyl-β-2-methylphenylpropionic acid (146·3 g., 95·2%), b. p. 110°/0·035 mm., 174°/15 mm., n_D^{18} 1·5202 (Found: C, 74·0; H, 8·0. Calc. for $C_{11}H_{14}O_2$: C, 74·1; H, 7·7%) (Bachmann *et al.*[25] give b. p. 179—180°/20 mm.) [p-*nitrobenzyl ester*, m. p. 65—65·5° (Found: C, 69·3; H, 6·3; N, 4·4. $C_{18}H_{19}O_4N$ requires C, 69·0; H, 6·1; N, 4·5%); amide, m. p. 109·5—110° (Found: C, 74·4; H, 8·6; N, 7·9. Calc. for $C_{11}H_{15}ON$: C, 74·5; H, 8·5; N, 7·9%) (Fusco and Rossi [3] give m. p. 95°)]; β-2 : 3-*dimethylphenylpropionic acid* (118·5 g., 77·7%), m. p. 116—117°) (Found: C, 74·1; H, 7·9%) [p-*bromophenacyl ester*, m. p. 89·5—90° (Found: C, 60·7; H, 5·1; Br, 21·4. $C_{19}H_{19}O_3Br$ requires C, 60·8; H, 5·1; Br, 21·3%); *amide*, m. p. 116—116·5° (Found: C, 74·3; H, 8·7; N, 8·2%)]; β-2 : 3-*dimethylphenyl-α-methylpropionic acid* (167 g., 87%), m. p. 72·5—73·5°, b. p. 124°/0·05 mm., 177°/15 mm. (Found: C, 74·9; H, 8·2. $C_{12}H_{16}O_2$ requires C, 74·9; H, 8·4%) [p-*bromophenacyl ester*, m. p. 79·5—80·0° (Found: C, 61·5; H, 5·3; Br, 21·8. $C_{20}H_{21}O_3Br$ requires C, 61·7; H, 5·4; Br, 21·5%); *amide*, m. p. 117·5—118° (Found: C, 75·3; H, 8·9; N, 7·5. $C_{12}H_{17}ON$ requires C, 75·3; H, 9·1; N, 7·3%)].

Substituted β-Phenylbutyric Acids.—2- or 4-Methylacetophenone (1·2 moles) and ethyl bromoacetate (1·3 moles) or ethyl α-bromopropionate (1·3 moles) in a mixture of benzene (400 c.c.) and toluene (300 c.c.) were allowed to react with zinc dust (1·5 g.-atoms) in the presence of mercuric bromide (5 g.) under reflux. After 2 hr. the solution was treated with 20% sulphuric acid (750 c.c.), and the organic phase was separated and washed with potassium hydrogen carbonate solution and with water until free from zinc salts. The solvent was evaporated, and the crude residue dehydrated by anhydrous formic acid (300 c.c.) at 80° for 1 hr. The product was isolated in the usual manner, and was fractionally distilled through a short Vigreux column. The following substituted cinnamic esters were obtained: ethyl 3-*p*-tolylbut-2-enoate (217·4 g., 83%), b. p. 158—164°/18 mm. (Found: C, 76·8; H, 7·7. Calc. for $C_{13}H_{16}O_2$: C, 76·4; H, 7·9%) (Ruzicka and Ehmann [4] give b. p. 158—160°/15 mm.); ethyl 2-methyl-3-*p*-tolylbut-2-enoate (213·7 g., 81·7%), b. p. 152—154°/18 mm. (Found: C, 76·9; H, 8·3. Calc. for $C_{14}H_{18}O_4$: C, 77·0; H, 8·3%) (lit.,[27] b. p. 141—141·5°/11 mm.); the *o*-tolyl isomer (25 g., 9·6%), b. p. 152—158°/20 mm. (lit.,[4] b. p. 128—132°/11 mm.), was hydrolysed directly to the *acid*, m. p. 160·5—161·5° (Found: C, 76·0; H, 7·4. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%) [p-*nitrobenzyl ester*, m. p. 89·5—90° (Found: C, 69·9; H, 5·8; N, 4·4. $C_{19}H_{19}O_4N$ requires C, 70·2; H, 5·9; N, 4·3%); *amide*, m. p. 161·5—162° (Found: C, 76·1; H, 7·8; N, 7·1. $C_{12}H_{15}ON$ requires C, 76·2; H, 8·0; N, 7·4%)]. Ethyl 3-*p*-tolylbut-2-enoate on hydrolysis gave the acid, m. p. 134—135° (Found: C, 75·1; H, 6·8. Calc. for $C_{11}H_{12}O_2$: C, 75·0; H, 6·9%) (lit.,[28] m. p. 134°) [p-*bromophenacyl ester*, m. p. 149—150° (Found: C, 61·2; H, 4·8; Br, 21·8. $C_{19}H_{17}O_3Br$ requires C, 61·1; H, 4·6; Br, 21·4%); *amide*, m. p. 130·5—131° (Found: C, 75·2; H, 7·6; N, 7·9. $C_{11}H_{13}ON$ requires C, 75·4; H, 7·5; N, 8·0%)]. The acid on catalytic hydrogenation (Raney nickel) gave β-*p*-tolylbutyric acid, m. p. 90·5—91·5° (Found: C, 74·4; H, 7·8. Calc. for $C_{11}H_{14}O_2$: C, 74·1; H, 7·9%) (lit.,[28] m. p. 91°) [p-*bromophenacyl ester*, m. p. 81—82° (Found: C, 60·8; H, 4·9; Br, 21·7. $C_{19}H_{19}O_3Br$ requires C, 60·8; H, 5·1; Br, 21·3%); *amide*, m. p. 120—121° (Found: C, 74·3; H, 8·4; N, 8·0. $C_{11}H_{15}ON$ requires C, 74·5; H, 8·5; N, 7·9%)]. Ethyl 2-methyl-3-*p*-tolylbut-2-enoate was hydrogenated over palladium, and the product was hydrolysed directly to α-methyl-β-*p*-tolylbutyric acid, m. p. 132·5—133·5° (Found: C, 74·9; H, 8·6. Calc. for $C_{12}H_{16}O_2$: C, 74·9; H, 8·4%) (lit.,[29] m. p. 133—133·5°) [p-*bromophenacyl ester*, m. p. 101·5—102° (Found: C, 61·4; H, 5·6; Br, 21·0. $C_{20}H_{21}O_3Br$ requires C, 61·7; H, 5·4; Br, 20·5%); *amide*, m. p. 139·5—140° (Found: C, 75·4; H, 9·1; N, 7·2. $C_{12}H_{17}ON$ requires C, 75·3; H, 9·0; N, 7·3%)].

Substituted Indanones.—The pure β-phenyl-propionic or -butyric acid (75—100 g.) was treated with anhydrous hydrogen fluoride (500—650 g.) in a closed copper vessel, fitted with a paraffin oil-sealed stirrer and an outlet tube and set aside with occasional gentle stirring at room temperature for 96 hr. The excess of hydrogen fluoride was evaporated, and the residue was neutralised with aqueous sodium acetate. The product was either extracted with ether and

[26] Hickinbottom and Porter, *J. Inst. Petroleum*, 1949, **35**, 629.
[27] Rupe, Steiger, and Fiedler, *Ber.*, 1914, **47**, 63.
[28] Rupe and Wiederkehr, *Helv. Chim. Acta*, 1924, **7**, 654.
[29] Campbell and Soffer, *J. Amer. Chem. Soc.*, 1942, **64**, 417.

fractionally distilled or, if solid, separated, steam-distilled, and crystallised from methanol. The following were obtained : 4-methylindanone (96·9%), m. p. 98—98·5° (Found : C, 82·2; H, 7·0. Calc. for $C_{10}H_{10}O$: C, 82·1; H, 6·9%) (lit.,[26] m. p. 97—98°) {2 : 4-dinitrophenylhydrazone, m. p. 284° (decomp.) (Found : C, 59·1; H, 4·2; N, 17·5. Calc. for $C_{16}H_{14}O_4N_4$: C, 59·9; H, 4·3; N, 17·2%) (lit.,[26] m. p. 280°); semicarbazone, m. p. 265—266° (decomp.) (Found : C, 65·0; H, 6·3; N, 20·5. Calc. for $C_{11}H_{13}ON_3$: C, 65·0; H, 6·5; N, 20·7%) [lit.,[30] m. p. 260° (decomp.)]}; 2 : 4-dimethylindanone (95·3%), m. p. 36—37°, b. p. 130—134°/14 mm. (Found : C, 82·4; H, 7·7. Calc. for $C_{11}H_{12}O$: C, 82·5; H, 7·6%) (lit.,[25] b. p. 147—149°/20 mm. [2 : 4-*dinitrophenylhydrazone*, m. p. 213—214° (Found : C, 59·8; H, 4·9; N, 16·4. $C_{17}H_{16}O_4N_4$ requires C, 60·0; H, 4·7; N, 16·5%); semicarbazone, m. p. 227—228° (decomp.) (Found : C, 66·0; H, 7·0; N, 19·1. Calc. for $C_{12}H_{15}ON_3$: C, 66·3; H, 7·0; N, 19·3%) (lit.,[25] m. p. 224—225°)]; 4 : 5-*dimethylindanone* (79%), m. p. 96·5—97° (Found : C, 82·7; H, 7·6. $C_{11}H_{12}O$ requires C, 82·5; H, 7·6%) [2 : 4-*dinitrophenylhydrazone*, m. p. 283—284° (Found : C, 59·8; H, 5·0; N, 16·3. $C_{17}H_{16}O_4N_4$ requires C, 60·0; H, 4·7; N, 16·5%); *semicarbazone*, m. p. 281—282° (decomp.) (Found : C, 65·7; H, 7·1; N, 19·5. $C_{12}H_{15}ON_3$ requires C, 66·3; H, 7·0; N, 19·3%); *oxime*, m. p. 204·5—205° (Found : C, 75·5; H, 7·5; N, 7·3. $C_{11}H_{13}ON$ requires C, 75·4; H, 7·5; N, 7·3%)]; 2 : 4 : 5-*trimethylindanone* (94·4%), m. p. 46—46·5°, b. p. 154°/11 mm. (Found : C, 82·5; H, 8·0. $C_{12}H_{14}O$ requires C, 82·7; H, 8·1%) [2 : 4-*dinitrophenylhydrazone*, m. p. 215—216° (Found : C, 60·8; H, 5·1; N, 15·4. $C_{18}H_{18}O_4N_4$ requires C, 61·0; H, 5·1; N, 15·8%); *semicarbazone*, m. p. 243—244° (decomp.) (Found : C, 67·6; H, 7·4; N, 18·0. $C_{13}H_{17}ON_3$ requires C, 67·5; H, 7·4; N, 18·2%)]; 3 : 6-dimethylindanone (94·3%), b. p. 130—134°/10 mm., n_D^{21} 1·5522 (Found : C, 82·5; H, 7·7. Calc. for $C_{11}H_{12}O$: C, 82·5; H, 7·6%) (lit.,[8] b. p. 100—102°/5 mm., n_D^{20} 1·5518) {2 : 4-dinitrophenylhydrazone, m. p. 271—272° (decomp.) (Found : C, 60·2; H, 4·8; N, 16·7. Calc. for $C_{17}H_{16}O_4N_4$: C, 60·0; H, 4·7; N, 16·5%) (lit.,[8] m. p. 271—273°); semicarbazone, m. p. 228—229° (decomp.) (Found : C, 66·4; H, 6·8; N, 19·4. Calc. for $C_{12}H_{15}ON_3$: C, 66·3; H, 7·0; N, 19·3%) [lit.,[8] m. p. 225° (decomp.)]}; 2 : 3 : 6-*trimethylindanone* (90%), b. p. 72—73°/0·15 mm., n_D^{20} 1·5407 (Found : C, 82·9; H, 8·2. $C_{12}H_{14}O$ requires C, 82·7; H, 8·1%) [2 : 4-*dinitrophenylhydrazone*, m. p. 207—208° (Found : C, 61·0; H, 5·1; N, 15·9. $C_{18}H_{18}O_4N_4$ requires C, 61·0; H, 5·1; N, 15·8%); *semicarbazone*, m. p. 210·5—211·5° (Found : C, 67·6; H, 7·4; N, 18·3. $C_{13}H_{17}ON_3$ requires C, 67·5; H, 7·4; N, 18·2%)].

3 : 4 : 7-*Trimethylindan*-1-*one*.—*p*-Xylene (n_D^{20} 1·4958; 80 g.) and crotonic acid (64·4 g.) were treated with anhydrous hydrogen fluoride (600 g.) in a closed copper vessel, and the solution was gently stirred for 30 min. and kept at room temperature for 96 hr. 3 : 4 : 7-Trimethylindanone (19 g., 14%), isolated in the usual manner, had m. p. 30—31°, b. p. 150—151°/17 mm. (Found : C, 82·5; H, 8·1. Calc. for $C_{12}H_{14}O$: C, 82·7; H, 8·1%) (lit.,[31] m. p. 32—33°, b. p. 146—148°/15 mm.) [*p*-nitrophenylhydrazone, m. p. 197—198° (Found : C, 69·5; H, 6·4; N, 13·5. Calc. for $C_{18}H_{19}O_2N_3$: C, 69·9; H, 6·2; N, 13·6%) (lit.,[31] m. p. 195°); 2 : 4-*dinitrophenylhydrazone*, m. p. 247·5—248·5° (Found : C, 61·0; H, 5·1; N, 15·9. $C_{18}H_{18}O_4N_4$ requires C, 61·0; H, 5·1; N, 15·8%)].

Oxidation of 4 : 5-*Dimethylindan*-1-*one*.—A suspension of the indanone (2·7 g.) in an excess of an alkaline solution of potassium permanganate (27 g.) was heated at 80° for 3½ hr. The product, isolated in the usual manner, had m. p. 231—232° (Found : C, 47·1; H, 2·5. Calc. for $C_{10}H_6O_8$: C, 47·3; H, 2·4%) (Fieser and Peters [32] give mellophanic acid, m. p. 236°) [Me_4 ester, m. p. 128° and mixed m. p. 128—129° (Found : C, 54·3; H, 4·7. Calc. for $C_{14}H_{14}O_8$: C, 54·2; H, 4·6%) (lit.,[32] m. p. 129—130°)].

Clemmensen Reduction of the Substituted Indanones.—The indanone (25 g.) in ethanol (125 c.c.) was slowly added to a boiling mixture of concentrated hydrochloric acid (105 c.c.), water (35 c.c.), ethanol (10 c.c.), and amalgamated zinc (100 g.) during 6 hr. Further acid (50 c.c.) was then slowly added. After 24 hr. the mixture was poured into water, and the product was isolated in the usual manner. The alkylindane was twice heated with potassium at 145—150° for 2 hr. and fractionated through a column (49 × 0·7 cm.) packed with stainless-steel gauze spirals (1/16 in.) [33] which had an efficiency greater than 25 theoretical plates at atmospheric pressure.[34] The fractions of constant b. p. were combined and distilled from sodium in order to

[30] Chakravarti, *J. Indian Chem. Soc.*, 1943, **20**, 393.
[31] Von Auwers and Risse, *Annalen*, 1933, **502**, 282.
[32] Fieser and Peters, *J. Amer. Chem. Soc.*, 1932, **54**, 4347.
[33] Dixon, *J. Soc. Chem. Ind.*, 1949, **68**, 88, 119.
[34] Quiggle and Fenske, *J. Amer. Chem. Soc.*, 1937, **59**, 1829.

remove traces of silicones dissolved from the tap-grease. The hydrocarbon was redistilled, and the receiver was sealed.

The following were obtained: 4-methylindane (21·1 g., 93·3%) (Found: C, 90·8; H, 9·2. Calc. for $C_{10}H_{12}$: C, 90·8; H, 9·2%) (lit.,[26] b. p. 203·9°/760 mm., n_D^{20} 1·5358); 2 : 4-*dimethylindane* (20·8 g., 91·1%) (Found: C, 90·5; H, 9·5. $C_{11}H_{14}$ requires C, 90·35; H, 9·65%); 4 : 5-*dimethylindane* (19·25 g., 84·3%) (Found: C, 90·5; H, 9·8%); 2 : 4 : 5-*trimethylindane* (21·3 g., 92·6%) (Found: C, 90·2; H, 10·0. $C_{12}H_{16}$ requires C, 89·9; H, 10·1%); 1 : 5-*dimethylindane* (20·9 g., 91·6%) (Found: C, 90·3; H, 9·6%); 1 : 2 : 5-*trimethylindane* (20·5 g., 89·2%) (Found: C, 89·9; H, 10·1%).

Reaction of Substituted Indanones with Methylmagnesium Iodide.—The indanone (25 g.) in ether (100 c.c.) was added during 1½ hr. to ethereal methylmagnesium iodide (from magnesium, 8 g.) cooled in ice. After a further hour at 0° the solution was heated under reflux for 1 hr. The product was decomposed with aqueous ammonium chloride, and the ethereal solution was separated, washed with water, dried ($MgSO_4$), and evaporated.

A modified procedure was followed for the reaction of 4-methyl- and 4 : 5-dimethyl-indanone, which partly underwent self-condensation in the presence of the Grignard reagent. The indanone (25 g.) in ether (800 c.c.) was added to the solution of methylmagnesium iodide during 5 hr., with efficient stirring and ice-cooling. After a further hour ether (750 c.c.) was distilled from the mixture, which was then treated as before.

In every experiment the 1-methylalkylindan-1-ol partly decomposed with the separation of water during the evaporation of the ether. Dehydration was completed by heating the product in benzene (100 c.c.) with aqueous 10% sulphuric acid (15 c.c.) at 80° for 1 hr. The solution was separated, washed with potassium hydrogen carbonate solution and with water, and evaporated. The residual alkylindene was either crystallised from methanol or distilled under reduced pressure. Hydrogenation over palladium at room temperature and 1 atmosphere gave the alkylindanes, which were purified as described above. The following were obtained: 1 : 4-dimethylindene (19·8 g., 78·1%), m. p. 14°, b. p. 105—107°/13 mm., n_D^{19} 1·5578; 1 : 4-*dimethylindane* (90·7%) (Found: C, 90·4; H, 9·8. $C_{11}H_{14}$ requires C, 90·35; H, 9·65%); 1 : 2 : 4-*trimethylindene* (21 g., 85%), m. p. 76·5—77·5° (Found: C, 90·8; H, 8·75. $C_{12}H_{14}$ requires C, 91·1; H, 8·9%) [*picrate*, m. p. 95·5—96° (Found: C, 55·6; H, 4·5; N, 10·9. $C_{18}H_{17}O_7N_3$ requires C, 55·8; H, 4·4; N, 10·9%)]; cis-1 : 2 : 4-*trimethylindane* (93·9%) (Found: C, 89·9; H, 10·1. $C_{12}H_{16}$ requires C, 89·9; H, 10·1%); 1 : 4 : 5-*trimethylindene* (19·6 g., 79·4%), m. p. 23—23·5°, b. p. 124—126°/14 mm., n_D^{25} 1·5579 (Found: C, 91·2; H, 8·9%); 1 : 4 : 5-*trimethylindane* (96%), (Found: C, 90·1; H, 10·0%); 1 : 2 : 4 : 5-*tetramethylindene* (21·4 g., 86·6%), m. p. 54—54·5° (Found: C, 90·6; H, 9·3. $C_{13}H_{16}$ requires C, 90·6; H, 9·4%) [*picrate*, m. p 94—94·5° (Found: C, 56·9; H, 4·8; N, 10·7. $C_{19}H_{19}O_7N_3$ requires C, 56·9; H, 4·8; N, 10·5%)]; cis-1 : 2 : 4 : 5-*tetramethylindane* (94·8%) (Found: C, 89·9; H, 10·4. $C_{13}H_{18}$ requires C, 89·6; H, 10·4%); 1 : 3 : 6-trimethylindene (19·6 g., 65%), b. p. 99·5—101·5°/10 mm., n_D^{20} 1·5461 (lit.,[35] b. p. 103—104°/14 mm., n_D^{20} 1·5478); 1 : 3 : 5-trimethylindane (92·8%) (Found: C, 89·8; H, 10·3%) (lit.,[35] b. p. 98—99°/14 mm., n_D^{20} 1·5206); 1 : 2 : 3 : 6-*tetramethylindene* (23·8 g., 92·6%), b. p. 122—126°/14 mm., n_D^{20} 1·5508 (Found: C, 90·9; H, 9·7%); 1 : 2 : 3 : 5-*tetramethylindane* (94·1%) (Found: C, 89·3; H, 10·7%).

1-*Alkylindanes.*—A solution of indan-1-one[36] (26·4 g., 0·2 mole) in ether (250 c.c.) was gradually added during 1½ hr. to a filtered solution of the alkyl-lithium[37] (0·3 mole) in ether (400 c.c.) with efficient stirring and cooling in ice–salt. After a further 30 min. the mixture was allowed to attain room temperature (1 hr.), then heated under reflux for 1 hr. The 1-alkylindanol was isolated in the usual manner and dehydrated without purification, by heating in benzene (100 c.c.) and aqueous 10% sulphuric acid (15 c.c.) at 80° for 1 hr. The product was isolated in the usual manner and distilled under reduced pressure. It was not possible to obtain a sharp separation of the 1-alkylindene from indan-1-one by this means, so the product was treated with Girard's reagent in methanol. The alkylindene was extracted with light petroleum and redistilled.

Hydrogenation of the 1-alkylindene over palladium at room temperature and pressure gave the 1-alkylindanes, which were purified as described above. The following were obtained: 1-butylindene (18·5 g., 53·8%), b. p. 134—136°/15 mm.; 1-*butylindane* (93·2%) (Found: C,

[35] Wagner-Jauregg and Hippchen, *Ber.*, 1943, **76**, 694.
[36] Ingold and Thorpe, *J.*, 1919, **115**, 143.
[37] Gilman, *J. Amer. Chem. Soc.*, 1949, **71**, 1499.

89·5; H, 10·4. $C_{13}H_{18}$ requires C, 89·6; H, 10·4%); 1-*hexylindene* (19·5 g., 48·8%), b. p. 164—165°/16 mm., n_D^{21} 1·5330 (Found: C, 90·0; H, 10·1. $C_{15}H_{20}$ requires C, 90·0; H, 10·0%); 1-*hexylindane* (Found: C, 88·9; H, 11·0. $C_{15}H_{22}$ requires C, 89·0; H, 11·0%).

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