147. *The Isomerisation of Aromatic Ketones through the Agency of Aluminium Chloride.*

By G. Baddeley and A. G. Pendleton.

The reaction between acetyldurene and excess of aluminium chloride at 100° provides a mixture of acetylprehnitene (80%), diacetyldurene (10%), and aromatic hydrocarbon (10%); 3 : 4 : 5-trimethylacetophenone (75%) and hexamethylbenzene (12%) were isolated from the products of interaction at 150°. At 100°, 9-acetyl-*s*-octahydroanthracene and 9-acetyl-*s*-octahydrophenanthrene afford 7-acetyl-2-methyl-4 : 5-*cyclo*hexenoindane (XVIII) in 75—80% yield. The mechanisms of the reactions are discussed.

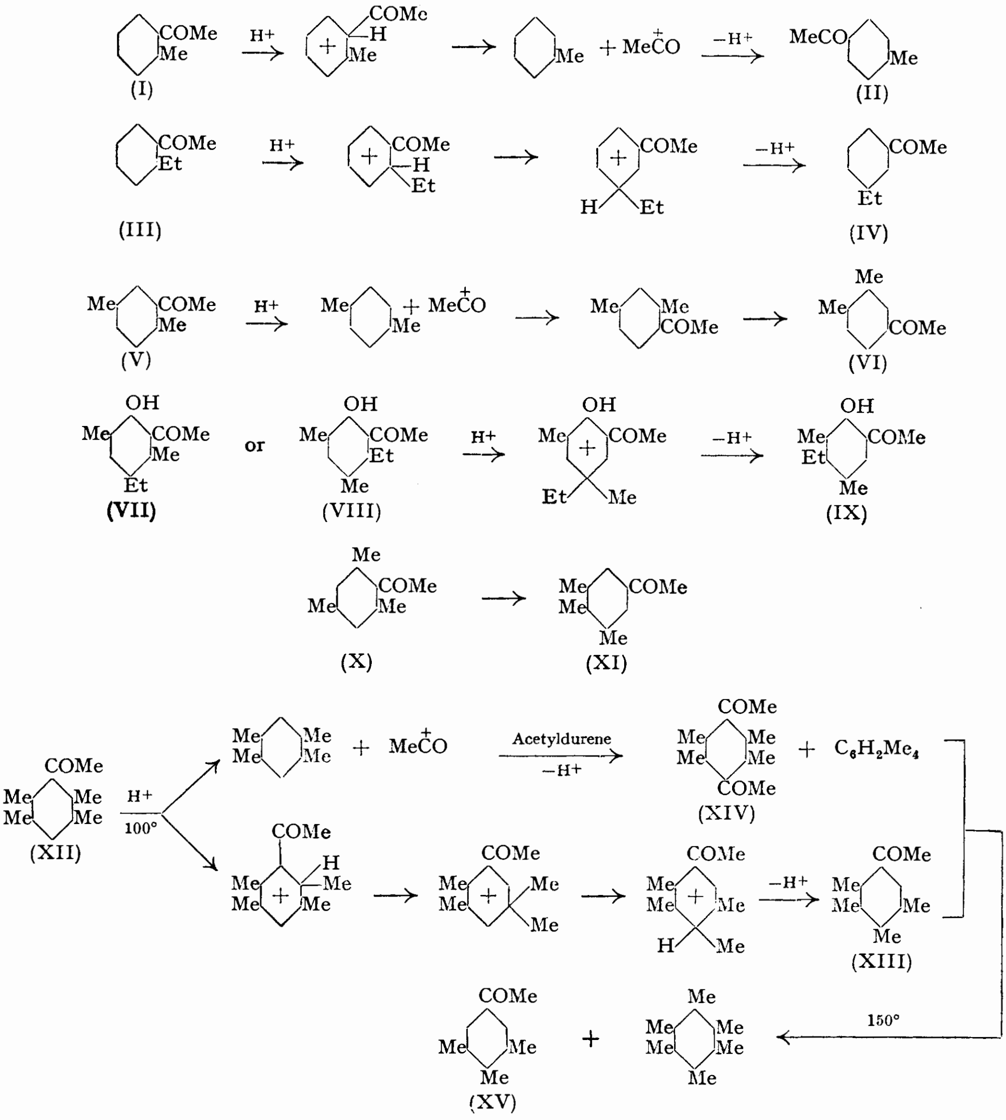
o-Alkylaryl ketones, in contrast to other alkylaryl ketones, become unstable at 80—150° in the presence of hydrogen halide and excess of aluminium halide and undergo a variety of irreversible changes which can be classified and illustrated as follows (*J.*, 1944, 232; 1950, 994) : (i) The ketone may suffer fission into aromatic hydrocarbon and an acyl cation which recombine to provide an isomeric ketone (I ⟶ II). (ii) The *ortho*-alkyl group may migrate intramolecularly to the adjacent *meta*-position (III ⟶ IV). (iii) Migration of the acyl group may provide an isomeric *o*-alkylaryl ketone which isomerises to the corresponding *m*-alkylaryl ketone (V ⟶ VI). (iv) The *ortho*-alkyl group may migrate to the neighbouring *meta*-position when this is already occupied by an alkyl group; the more mobile alkyl group will then migrate to the *para*-position (VII and VIII ⟶ IX; Auwers, *Annalen*, 1928, **460**, 254). (v) In *oo*′-dialkylaryl ketones, both *ortho*-alkyl groups may migrate to the corresponding *meta*-positions (X ⟶ XI). In all instances, one molecular proportion of aluminium halide combines with the carbonyl group to form an oxonium complex, and additional aluminium halide is needed to effect isomerisation.

Up to the present, the aromatic ketones which have been isomerised through the agency of aluminium halide have contained two or more unsubstituted positions in the benzene ring and have provided ketones which have only hydrogen atoms in the positions *ortho* to the carbonyl group. We now report the action of aluminium chloride on three ketones, acetyldurene (2 : 3 : 5 : 6-tetramethylacetophenone) and 9-acetyl-*s*-octahydroanthrancene and -phenanthrene, which have only one nuclear position occupied by a hydrogen atom.

At 100°, acetyldurene (XII) afforded acetylprehnitene(2 : 3 : 4 : 5-tetramethylacetophenone) (XIII) (80%), diacetyldurene (XIV) (10%), and hydrocarbon (10%). The last two arise from fission of acetyldurene into durene and acetyl cation; as a consequence of steric inhibition of conjugation between acetyl group and benzene ring (*Nature*, 1939, **144**, 444; Meyer, *Ber.*, 1895, **28**, 3213; 1896, **29**, 848, 2564) acetyldurene readily affords diacetyldurene by acetylation. Acetylprehnitene, on the other hand, is the product of intramolecular displacement of one of the *o*-methyl groups.

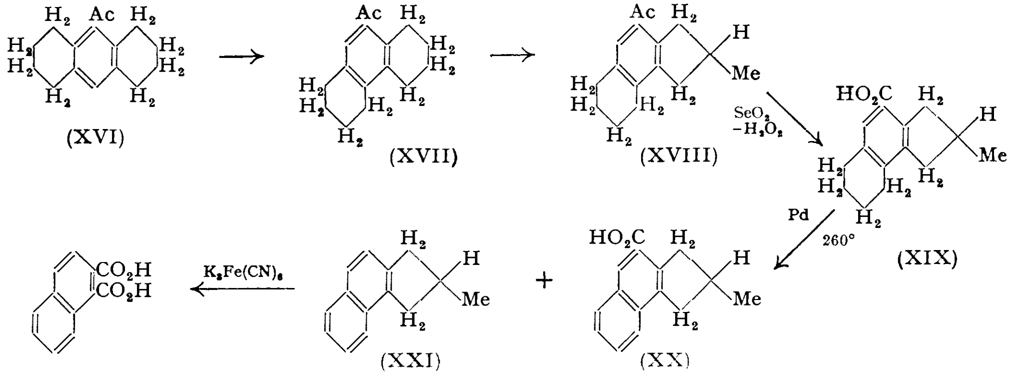
5-Acetylhemimellitene (3 : 4 : 5-trimethylacetophenone) (XV) (75%) and hexamethylbenzene (12%) were isolated from the products of interaction at 150°; they arise from demethylation of acetylprehnitene by aromatic hydrocarbon, for this ketone in the absence of aromatic hydrocarbon is unaffected by excess of aluminium chloride at 150°. The demethylation of *p*-cresol by aromatic hydrocarbon has been reported previously by one of us (*J.*, 1943, 527).

At 100°, 9-acetyl-*s*-octahydroanthracene (XVI) afforded an isomeric ketone; the following data show this to be 7-acetyl-2-methyl-4 : 5-*cyclo*hexenoindane (XVIII): (i) It readily provided a semicarbazone and therefore, unlike (XVI), has a carbonyl group which

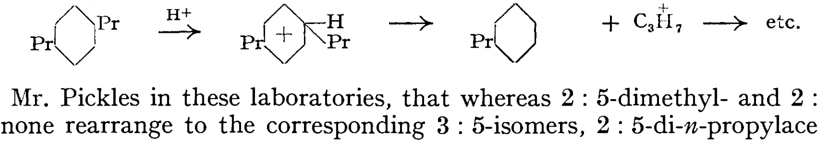


(All the rings are aromatic.)

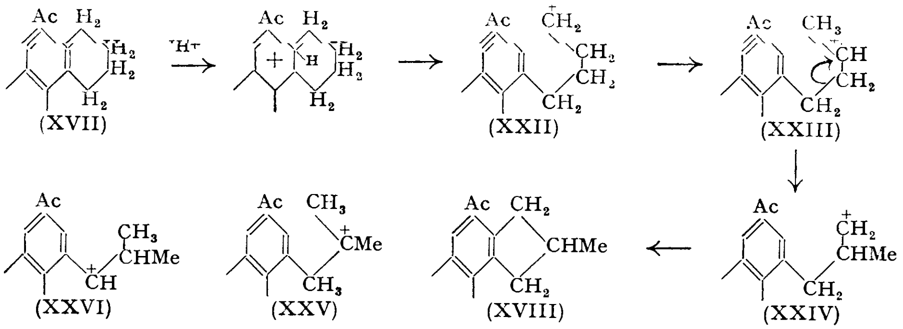
is not sterically hindered. (ii) It is a methyl ketone, as oxidation by selenium dioxide provided a glyoxal derivative which afforded an acid $C_{14}H_{17}{\cdot}CO_2H$ (XIX) in the presence of alkaline hydrogen peroxide. (iii) This acid evolved two molecular equivalents of hydrogen when heated with palladium at 260° and therefore has only one tetrahydrogenated aromatic ring; the other products of this reaction were an acid $C_{14}H_{13}{\cdot}CO_2H$ (XX) and a hydrocarbon $C_{14}H_{14}$ (XXI). (iv) The acid $C_{14}H_{17}{\cdot}CO_2H$ has one methyl group, as oxidation by chromic acid (Kuhn and Roth, *Ber.*, 1933, **66**, 1274) provided acetic acid (0·83 mol.). (v) The hydrocarbon $C_{14}H_{14}$ afforded naphthalene-1 : 2-dicarboxylic acid on oxidation with potassium ferricyanide and was thereby identified as 1-, 2- or 3-methyl-4 : 5-benzindane. (vi) These three hydrocarbons were synthesised. 1- and 2-Methyl-4 : 5-benzindane were obtained by Clemmensen reduction of 1- and 2-methyl-4 : 5-benzindan-3-one which, in turn, were prepared as described by Pfeiffer, Jenning, and Stöcker (*Annalen*, 1949, **563**, 73) and Cook, Dansi, Hewett, Iball, Mayneord, and Roe (*J.*, 1935, 1324) respectively. 3-Methyl-4 : 5-benzindane was obtained by addition of methylmagnesium iodide to 4 : 5-benzindan-3-one, derived from β-2-naphthylpropionic acid as described by Ansell and Hey (*J.*, 1950, 2874), and reduction of the resulting 3-methyl-4 : 5-benzindan-3-ol by hydriodic acid. We prepared β-2-naphthylpropionic acid from 2-naphthylmethyl bromide; our sample of 2-naphthylmethylmalonic acid melted at 147—148° (Found: C, 69·2; H, 4·9. Calc. for $C_{14}H_{12}O_4$: C, 68·9; H, 4·9%) and not at 94—95° as recorded by Meyer and Sieglitz (*Ber.*, 1922, **55**, 1835). These three methyl derivatives of 4 : 5-benzindane form crystalline complexes with picric acid and 1 : 3 : 5-trinitrobenzene; the melting points of these derivatives and those of 4 : 5-benzindane and the hydrocarbon $C_{14}H_{14}$ are assembled in the Table on p. 811; they clearly indicate that the last-mentioned is 2-methyl-4 : 5-benzindane and this was confirmed by mixed-melting-point determinations. (vii) 9-Acetyl-*s*-octahydrophenanthrene (XVII) provides the same isomeric ketone (XVIII) as does 9-acetyl-*s*-octahydroanthracene, whereas 6-acetyltetralin is unaffected by aluminium chloride at 100°; therefore, in 9-acetyl-*s*-octahydrophenanthrene, the tetrahydrogenated six-membered ring adjacent to the carbonyl group is the one which contracts to a five-membered ring and the product is 7-acetyl-2-methyl-4 : 5-*cyclo*hexenoindane (XVIII).



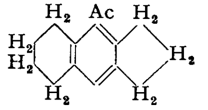
The isomerisation of 9-acetyl-*s*-octahydroanthracene to the corresponding phenanthrene derivative (XVI ⟶ XVII) is analogous to that of acetyldurene to acetylprehnitene. The isomerisation of 9-acetyl-*s*-octahydrophenanthrene to 7-acetyl-2-methyl-4 : 5-*cyclo*hexenoindane (XVII ⟶ XVIII) under conditions which do not affect acetylprehnitene was not unexpected as work in these laboratories has demonstrated that, in the interaction of aromatic ketones with aluminium halide, the methyl group is less mobile than are other alkyl groups; a possible explanation of this isomerisation arises from the observation,



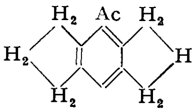
made by Mr. Pickles in these laboratories, that whereas 2 : 5-dimethyl- and 2 : 5-diethylacetophenone rearrange to the corresponding 3 : 5-isomers, 2 : 5-di-*n*-propylacetophenone suffers considerable disproportionation into 3-*n*-propylacetophenone (35%) and more highly alkylated acetophenones; apparently, the 2-propyl group can be ejected as the propyl or *iso*propyl cation. Should the *cyclo*hexeno-group adjacent to the carbonyl group in 9-acetyl-*s*-octahydrophenanthrene behave similarly, the following changes become possible :



(XVII) (XXII) (XXIII) (XXVI) (XXV) (XVIII) (XXIV)

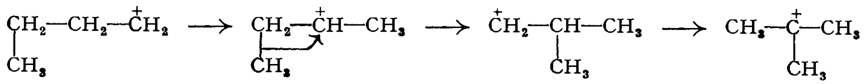


(XXVII)



(XXVIII)

The primary carbonium ion (XXII) rearranges to the secondary carbonium ion (XXIII) which, by a Wagner–Meerwein transformation, provides (XXIV). This cation, though less stable than either (XXV) or (XXVI), is the only one of these three which can provide ring closure; the product is (XVIII). The formation and rearrangement of (XXII), though speculative, have a precedent in the isomerisation of benzene homologues in the presence of aluminium halide; for example, a *n*-butyl group can provide a *sec.*-butyl group and the latter a *tert.*-butyl group; these rearrangements occur in the alkyl cation and have been formulated by Nightingale and Smith (*J. Amer. Chem. Soc.*, 1939, **61**, 101) as :



$$\underset{CH_3}{CH_2}-CH_2-\overset{+}{C}H_2 \longrightarrow \underset{CH_3}{CH_2}-\overset{+}{C}H-CH_3 \longrightarrow \overset{+}{C}H_2-\underset{CH_3}{CH}-CH_3 \longrightarrow CH_3-\underset{CH_3}{\overset{+}{C}}-CH_3$$

The instability of *o*-alkylaryl ketones in the presence of excess of aluminium halide is a consequence of steric interaction between the acyl and vicinal alkyl groups (*idem, ibid.*) and, undoubtedly, the isomerisation of 9-acetyl-*s*-octahydrophenanthrene to 7-acetyl-2-methyl-4 : 5-*cyclo*hexenoindane provides a decrease in this type of steric interaction. Evidence of the decrease in steric interaction which accompanies the replacement of a six- by a five-membered ring in compounds of this type has been obtained on previous occasions; for example, application of Raman spectra and interaction with methylmagnesium bromide and alkaline hypochlorite, respectively, have demonstrated that steric hindrance decreases in the series 9-acetyloctahydroanthracene > 4-acetyl-5 : 6-*cyclo*hexenoindane (XXVII) > 4-acetyl-*s*-hydrindacene (XXVIII) (Arnold and Rondestvedt, *ibid.*, 1946, **68**, 2176; 1945, **67**, 1265; Arnold and Craig, *ibid.*, 1948, **70**, 2791).

EXPERIMENTAL

Acetyldurene and Aluminium Chloride.—(a) *At* 100°. The ketone (7·5 g.), the chloride (15 g.), and sodium chloride (1 g.) were heated together for 2 hours; distillation of recovered organic material provided fractions (i), b. p. 90—120°/20 mm. (0·8 g.) and (ii) b. p. 130—140°/20 mm. (5·9 g.), and a residue (0·8 g.) which solidified on cooling and provided pure diacetyldurene (m. p. and mixed m. p. 178—179°) after recrystallisation from ethanol. Fraction (i) had the physical properties (b. p. 204°; m. p. —4°) of prehnitene but is probably a mixture of aromatic hydrocarbons as nitration by cold concentrated nitric–sulphuric acids provided a product, m. p. 152—162°, which was unaffected by recrystallisation; dinitroprehnitene melts at 178° (Jacobsen, *Ber.*, 1886, **19**, 1209; Smith and Cass, *J. Amer. Chem. Soc.*, 1932, **54**, 1614) and dinitrodurene at 205° (Nef, *Annalen*, 1887, **237**, 4). On a subsequent occasion, this hydrocarbon fraction was found to contain hexamethylbenzene (m. p. and mixed m. p. 165—166°). Fraction (ii) was identified as acetylprehnitene [*semicarbazone*, m. p. and mixed m. p. 209° (Found : N, 18·5. $C_{13}H_{19}ON_3$ requires N, 18·0%)]; alkaline hypochlorite oxidised it to 2 : 3 : 4 : 5-tetramethylbenzoic acid (m. p. and mixed m. p. 165°).

(b) *At* 150°. A mixture of the ketone (7·5 g.), aluminium chloride (15 g.), and sodium chloride (1 g.) was fused at 100° and the orange-red melt heated at 150° for 3 hours. The recovered organic material, b. p. 135—140°/20 mm. (6·0 g.), was a mixture of oil (5·2 g.) and solid (0·8 g.) and was filtered. The solid crystallised from ethanol in colourless prisms, m. p. 165—166° (Found: C, 88·4; H, 11·1. Calc. for $C_{12}H_{18}$: C, 88·9; H, 11·1%). Jacobsen (*loc. cit.*) and Smith and Cass (*loc. cit.*) give m. p. 166° for hexamethylbenzene. The oil was identified as 3 : 4 : 5-trimethylacetophenone (semicarbazone, m. p. and mixed m. p. 217°). Subsequently, the hydrocarbon and ketonic components were separated by dissolving the mixture in light petroleum and extracting it with 80% sulphuric acid in which ketonic material is readily soluble.

Acetylprehnitene and Aluminium Chloride at 150°.—The ketone was recovered unchanged after 3 hours.

9-*Acetyl*-s-*octahydroanthracene and Aluminium Chloride*.—The ketone (50 g.), the chloride (76 g.) and sodium chloride (3 g.) were heated together at 100° for 2 hours. The organic product, b. p. 148°/0·12 mm. (45 g.), consisted of a solid, 7-*acetyl*-2-*methyl*-4 : 5-cyclo*hexenoindane* (see below) (30·2 g.), and an oil (14·8 g.) which were separated by filtration. The solid crystallised from ethanol in bundles of slender colourless needles, m. p. 97—98° (Found : C, 83·9; H, 8·7. $C_{16}H_{20}O$ requires C, 84·2; H, 8·8%). A sample of the oil (5·0 g.) was heated at 100° for 2 hours with aluminium chloride (8 g.) and sodium chloride (1 g.) and provided a further sample of the solid, m. p. 97—98° (1·5 g.), and oil (2·4 g.).

The solid formed a *semicarbazone* which crystallised from ethanol in needles, m. p. 154—155° (Found : N, 15·0. $C_{17}H_{23}ON_3$ requires N, 14·8%), and an *oxime* which crystallised from methanol in prisms, m. p. 154—155° (Found : N, 5·7. $C_{16}H_{21}ON$ requires N, 5·8%).

The solid (5 g.) was added to a stirred solution of selenium dioxide (2·5 g.) in water (0·5 c.c.) and dioxan (34 c.c.) at 55°, and the mixture was boiled under reflux for 4 hours. The precipitated selenium was separated by filtration and the filtrate cooled and diluted with water. The glyoxal derivative separated as a white solid, m. p. 107—112° (5·7 g.). A sample (4 g.) was dissolved in ethanol (60 c.c.) and aqueous hydrogen peroxide (30%; 20 c.c.), and 10% sodium hydroxide solution was added dropwise until reaction was complete. The resulting solution was warmed to 80° for 30 minutes, diluted with water, decolourised with animal charcoal, cooled, and acidified with concentrated hydrochloric acid. The precipitated 2-*methyl*-4 : 5-cyclo*hexenoindane*-7-*carboxylic acid* was separated, washed with water, dried, and recrystallised from ethanol. The acid (3·3 g.) melted at 207—208° [Found : C, 78·5; H, 7·9; Me (Kuhn–Roth), 5·4. $C_{15}H_{18}O_2$ requires C, 78·3; H, 7·8; 1Me, 6·5%].

This acid (5·0 g.) was heated with palladised charcoal (2 g.) at 260° in a slow stream of carbon dioxide. Hydrogen (922 c.c. Calc. for four atoms : 975 c.c.) was collected in 6 hours. The reaction mixture was cooled and extracted with ether and the extract washed with 2N-sodium hydroxide and dried (K_2CO_3). The alkaline washings were acidified and provided 2-*methyl*-4 : 5-*benzindane*-7-*carboxylic acid*, needles (0·7 g.), m. p. 230—232°, from ethanol (Found: C, 79·7; H, 6·2. $C_{15}H_{14}O_2$ requires C, 79·7; H, 6·2%). The ethereal extract provided 2-*methyl*-4 : 5-*benzindane* (2·0 g.), b. p. 127°/0·2 mm. (Found: C, 92·1; H, 7·9. $C_{14}H_{14}$ requires C, 92·3; H, 7·7%). This hydrocarbon formed a *picrate* and an addition *compound* with 1 : 3 : 5-trinitrobenzene, for which see the Table.

A mixture of the above hydrocarbon $C_{14}H_{14}$ (0·4 g.) and a solution of potassium ferricyanide (25 g.) and potassium hydroxide (4·3 g.) in water (90 c.c.) was vigorously stirred at 60° for

	Picrate			s-$C_6H_3(NO_2)_3$ compound		
		Found, %,[a]			Found, %,[b]	
Parent compound	M. p.	C	H	M. p.	C	H
4 : 5-Benzindane	109—110° [c]	—	—	119—120°	60·2	3·6
1-Methyl-4 : 5-benzindane	88—89	58·2	4·0	88—89	61·0	4·1
2-Methyl-4 : 5-benzindane	90·5—91 [d]	—	—	103·5—104 [e]	—	—
3-Methyl-4 : 5-benzindane	108—109	58·1	4·1	114—115	61·4	4·5
Hydrocarbon $C_{14}H_{14}$	90·5—91 [d]	58·3	4·1	103·5—104 [e]	61·1	4·1

[a] For the alkyl derivatives, $C_{20}H_{17}O_7N_3$ requires C, 58·4; H, 4·1%. [b] For 4 : 5-benzindane, $C_{19}H_{15}O_6N_3$ requires C, 59·8; H, 3·9%. For the alkyl derivatives, $C_{20}H_{17}O_6N_3$ requires C, 61·1; H, 4·3%. [c] Kruber (*Ber.*, 1932, **65**, 1388) records 110°. [d, e] No depression on admixture of pairs.

24 hours. Most of the oil had now disappeared and the remainder was removed with steam. The reaction mixture was cooled and filtered and the filtrate carefully acidified. The precipitate crystallised from acetic acid in slender colourless needles (0·2 g.), m. p. 166—167° (Found : C, 72·6; H, 3·0. Calc. for $C_{12}H_6O_3$: C, 72·7; H, 3·0%), and did not depress the m. p. [166—167°; Kruber (*loc. cit.*) gives m. p. 163—164°] of naphthalene-1 : 2-dicarboxylic anhydride obtained from 4 : 5-benzindane by the above procedure.

3-*Methyl*-4 : 5-*benzindane*.—4 : 5-Benzindan-3-one (4 g.) in ether was gradually added to a solution of magnesium (1·35 g.) in methyl iodide (6·25 g.) and ether (50 c.c.). After being kept overnight, the mixture was poured on ice and acidified with ammonium chloride and a little dilute sulphuric acid. The ethereal extract was washed with sodium carbonate solution, then dried (K_2CO_3), and the ether removed at room temperature under reduced pressure. The crystalline residue of 3-*methyl*-4 : 5-*benzindan*-3-*ol* crystallised from ether in small colourless prisms (4·2 g.), m. p. 117—118° (Found : C, 84·3; H, 7·4. $C_{14}H_{14}O$ requires C, 84·8; H, 7·1%). A mixture of the alcohol (3·25 g.), hydriodic acid (10 c.c.; *d* 1·7), and red phosphorus (1 g.) was boiled under reflux in an atmosphere of nitrogen for 3 hours; it was then diluted with water and extracted with ether, the ethereal extract filtered and washed with sodium thiosulphate solution, and the ether removed. The residue was distilled with steam and provided 3-methyl-4 : 5-benzindane (0·8 g.).

2-*Methyl*-4 : 5-*benzindane*.—This hydrocarbon (2·7 g.) was obtained by Clemmensen reduction of 2-methyl-4 : 5-benzindan-3-one (5·2 g.).

1-*Methyl*-4 : 5-*benzindane*.—This (0·85 g.) was obtained by Clemmensen reduction of 1-methyl-4 : 5-benzindan-3-one (1·75 g.).

The *picrates* and the addition *compounds* with 1 : 3 : 5-trinitrobenzene of the three isomers crystallised from ethanol (see Table). 4 : 5-Benzindane gave an addition *compound* with 1 : 3 : 5-trinitrobenzene (see Table).

9-*Acetyl*-s-*octahydrophenanthrene and Aluminium Chloride*.—These components (5 g. and 8 g. respectively) and sodium chloride (1 g.) were fused together at 100° for 2 hours and provided 7-acetyl-2-methyl-4 : 5-benzindane (2·7 g.), m. p. and mixed m. p. 97—98°, and an oil (0·9 g.), b. p. 160°/0·5 mm.

6-*Acetyltetrahydronaphthalene and Aluminium Chloride*.—These components (9 g. and 18 g. respectively) and sodium chloride (1 g.) were fused together at 100° for 2 hours. The ketone (7·5 g.), b. p. 150°/15 mm. (oxime, m. p. and mixed m. p. 106—107°), was recovered unchanged. The oxime separated from ethanol in crystals, m. p. 85°, and reverted to crystals, m. p. 106—107°, on storage.

We are indebted to Professor J. W. Cook, F.R.S., and to Imperial Chemical Industries Limited, Dyestuffs Division, for gifts of *s*-octahydrophenanthrene and *s*-octahydroanthracene respectively, and to Mr. R. Williamson for valuable help in the study of the isomerisation of acetyldurene.

FACULTY OF TECHNOLOGY, UNIVERSITY OF MANCHESTER. [*Received, November* 12*th*, 1951.]