890. *Friedel–Crafts Acylation and Alkylation. A Comparison of Inter- and Intra-molecular Processes.*

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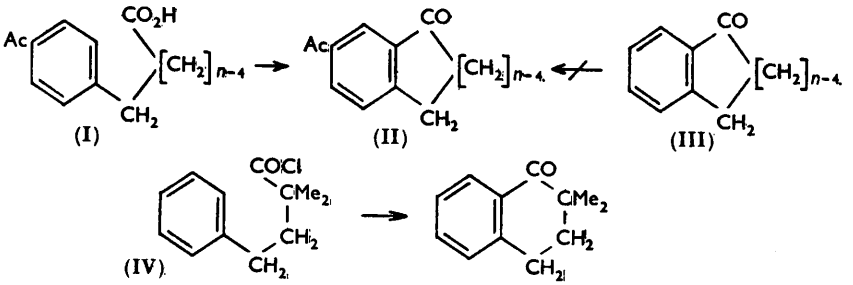
The following comparisons are illustrated and discussed : (i) Phenyl groups which are deactivated towards electrophilic substitution by carboxyl or acyl substituents and thereby made incapable of undergoing intermolecular acylation may participate in intramolecular acylation if this provides a 5- or 6-membered ring. (ii) Intramolecular alkylation which involves the formation of a 5-, 6-, or 7-membered ring is less affected by isomerisation of the alkylating agent than is intermolecular alkylation and provides ready primary alkylation of a phenyl group which has an acyl substituent. (iii) Cyclisation of halogenoalkyl phenyl ketones occurs more readily and is less affected by isomerisation than is that of *p*-chloroalkylacetophenones.

It is well known that intramolecular reactions effecting the formation of five- and six-membered rings occur more readily than the corresponding intermolecular processes. This paper illustrates the major differences between inter- and intra-molecular acylation and alkylation of phenyl groups by the Friedel–Crafts process and the effect thereon of replacing phenyl by acetylphenyl groups.

Acylation.—Intermolecular acylation of monoalkylbenzenes affords only monoacyl derivatives and attempts to enforce diacylation, *e.g.*, by raising the temperature, usually cause (*a*) decomposition of the acylating agent and (*b*) dehydrogenation of the alkyl substituent (forthcoming communication). For example, reaction of acetylating agent with 4-ethylacetophenone requires a temperature of *ca.* 100° and gives (*a*) acetylacetone and other products of decomposition of the acetylating agent, and (*b*) *p*-acetylbenzylideneacetone, the final product of the interaction of the acylating agent and the ethyl substituent: $p\text{-Ac}\cdot C_6H_4\cdot CH_2\cdot CH_3 + Me\cdot COCl,AlCl_3 \longrightarrow HCl + Me\cdot CHO,AlCl_3 + p\text{-Ac}\cdot C_6H_4\cdot CH{:}CH_2$ $\xrightarrow{Me\cdot COCl,AlCl_3}$ $p\text{-Ac}\cdot C_6H_4\cdot CH{:}CHAc$.

On the other hand, intramolecular acylation of aromatic ketones is comparatively easy : *e.g.*, whereas indan-1-one and 1-tetralone (III; $n = 5$ and 6 respectively) cannot be acetylated, their acetyl derivatives (II) are readily obtained by cyclisation of β-*p*-acetylphenylpropionic (I; $n = 5$) and γ-*p*-acetylphenylbutyric acid (I; $n = 6$) through the agency of aluminium chloride.[1] Similarly, the dicarboxylic acids obtained by hypochlorite oxidation of the keto-acids (I; $n = 5$ and 6) are readily converted into 1-oxoindane-6-carboxylic acid and 1-tetralone-7-carboxylic acid respectively.[1]

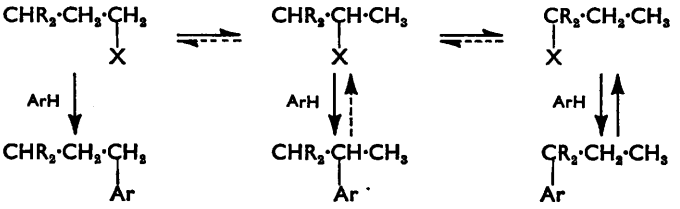


In further illustration of the comparative ease of intramolecular acylation is the fact that the decarbonylation process, $RR'R''C\cdot COCl,AlCl_3 \longrightarrow RR'R''CCl,AlCl_3 + CO$, which interrupts the Friedel–Crafts acylation of benzene and its derivatives by tertiary acid chlorides, is of no account in the cyclisation of αα-dimethyl-γ-phenylbutyryl chloride (IV). However, this process is interrupted by decarbonylation when the reactivity of the phenyl groups towards acylating agent is low : thus carbon monoxide is evolved in the reaction of αα-dimethyl-γ-*p*-acetylphenylbutyryl chloride (VII) with aluminium chloride; the other

[1] See Experimental section.

product, 7-acetyl-1 : 2 : 3 : 4-tetrahydro-2-methylnaphthalene (VI), is afforded by intramolecular primary alkylation.[1]

Alkylation.—Isomerisation of the alkylating agent is a feature of the Friedel–Crafts alkylation of benzene and its homologues, and the products of monoalkylation are determined (*a*) by the relative rates of the several reactions indicated in the scheme below and (*b*) by the extent to which the reaction mixture is allowed to approach equilibrium composition.



Some of the more important considerations are: (i) Alkyl halide readily isomerises in the direction primary ⟶ secondary ⟶ tertiary; reversal of these changes is less ready. (ii) The reactivity of alkyl cation as electrophilic reagent decreases in the order primary > secondary > tertiary. (iii) Ease of reversal of the alkylation process increases in the order primary < secondary < tertiary; in fact, primary alkylation at room temperature is irreversible. (iv) Acetophenone is much less reactive towards alkylating agent than is benzene and attempts to alkylate the former provide (*a*) considerable, and in the case of tertiary alkylating agent complete, decomposition of the agent and (*b*) greater opportunity for the isomerisation of the agent. For example, *n*-propyl halide, *n*-propyl alcohol, and di-*n*-propyl ether severally in the presence of aluminium chloride effect only *iso*propylation of acetophenone; the product is 3-*iso*propylacetophenone.[2]

In general, alkylation of benzene with primary alkyl halide gives a mixture of primary and secondary alkylbenzene, and tertiary alkyl halide effects mainly secondary alkylation.[3] These generalisations do not apply to the corresponding intramolecular processes; these are comparatively fast and isomerisation is consequently less important. Thus each of the phenylalkyl chlorides, be it primary, secondary or tertiary, listed in Table 1 underoges ring closure without isomerisation.[1] The preparation of benzosuberane from 1-chloro-5-phenylpentane is noteworthy since this chloride is reported[4] as giving phenyl*cyclo*pentane.

These straightforward ring closures can no longer be effected after the reactivity of the phenyl group as a nucleophile has been decreased by acetylation.[1] Each of the chloroalkylacetophenones listed in Table 2 gives 5-acetyl-2-alkylindane on fusion with excess of aluminium chloride–sodium chloride at 100°. In each instance the final product is afforded by intramolecular primary alkylation; *i.e.*, it involves the most reactive alkylating agent and the least reversible process. The isomerisations of the chloroalkyl side-chains probably involve the following rearrangements:

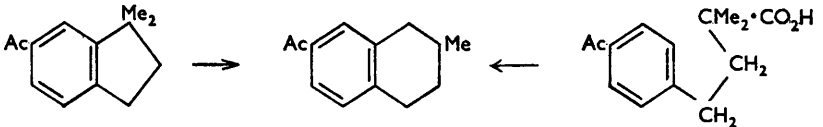
(i) —CH_2·CH_2·CH_2Cl ⟶ —CH_2·$CHCl$·CH_3 ⟶ —$CHCl$·CH_2·CH_3

as in (*D*) ⟶ (*E*) ⟶ (*F*) (see Table 2), a well-known phenomenon, and (ii) migration of a 4-acetylbenzyl group in the Wagner–Meerwein rearrangement of aralkyl cation as in (*B*) ⟶ (*C*) (see Table 2):

Should ring closure be effected by tertiary alkylation the product would be unstable: it is shown[1] that 6-acetyl-1 : 1-dimethylindane (V) gives 7-acetyl-2-methyltetralin (VI), the same product as is afforded by αα-dimethyl-γ-*p*-acetylphenylbutyric acid (VII), by fusion with aluminium chloride.

[1] Unpublished work.
[2] Baddeley, *Quart. Rev.*, 1954, **8**, 355.
[4] Von Braun and Deutsch, *Ber.*, 1912, **45**, 1271, 2178.

Whereas the ketone (VI), like 6-acetyltetralin, is stable towards excess of aluminium chloride, alicyclic rings which are adjacent to an acetyl group in a benzene ring are readily



(V) (VI) (VII)

opened even when this process involves the formation of a primary alkyl cation. This instability is illustrated by the isomerisation of 9-acetyl-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydro-

TABLE 1.

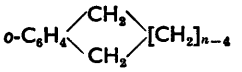
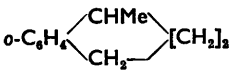
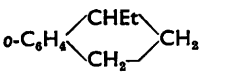
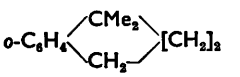
Ph·CH$_2$·[CH$_2$]$_{n-4}$·CH$_2$Cl (n = 5, 6, and 7)	
Ph·CH$_2$·CH$_2$·CH$_2$·CHCl·Me	
Ph·CH$_2$·CH$_2$·CHCl·Et	
Ph·CH$_2$·CH$_2$·CH$_2$·CMe$_2$Cl	

TABLE 2.

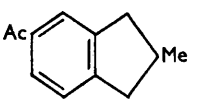
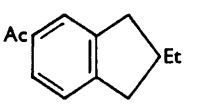
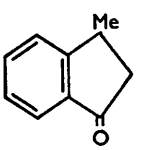
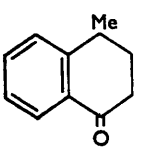
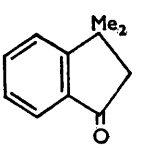
(*A*) *p*-Ac·C$_6$H$_4$·CH$_2$·CH$_2$·CH$_2$·CH$_2$Cl	⟶	
(*B*) *p*-Ac·C$_6$H$_4$·CH$_2$·CH$_2$·CHCl·Me	⟶	
(*C*) *p*-Ac·C$_6$H$_4$·CH$_2$·CHMe·CH$_2$Cl	⟶	
(*D*) *p*-Ac·C$_6$H$_4$·CH$_2$·CH$_2$·CH$_2$·CH$_2$·CH$_2$Cl	⟶	
(*E*) *p*-Ac·C$_6$H$_4$·CH$_2$·CH$_2$·CH$_2$·CHCl·Me	⟶	
(*F*) *p*-Ac·C$_6$H$_4$·CH$_2$·CH$_2$·CHCl·Et	⟶	

TABLE 3.

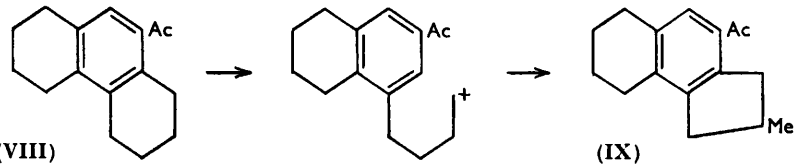
Ph·CO·CH$_2$·CH$_2$·CH$_2$Br	
Ph·CO·CH$_2$·CH$_2$·CHBr·Me	
Ph·CO·CH$_2$·CMe$_2$·CO$_2$H	

phenanthrene (VIII) ⟶ (IX) : [5] rupture of an alicyclic ring occurs and is followed by a series of rearrangements similar to those discussed above [Table 2, (*A*) ⟶ (*B*) ⟶ (*C*)]

[5] Baddeley and Pendleton, *J.*, 1952, 807.

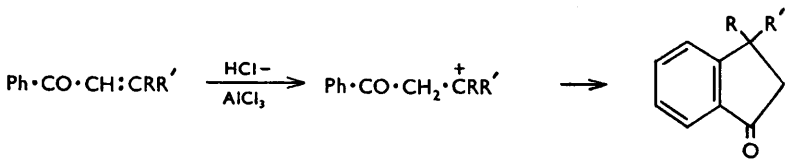
and reaction is completed by intramolecular primary alkylation with formation of a five-membered ring.

Ring closure of phenyl halogenoalkyl ketones occurs more readily than that of the above chloroalkylacetophenones : as shown by the data [1] in Table 3, it can be effected by intra-



(VIII) (IX)

molecular secondary and tertiary alkylation. These reactions are similar to those effecting ring closure of aryl vinyl ketones;[3] these compounds combine with a proton and then undergo intramolecular alkylation : *e.g.*,



Experimental

Intramolecular Acylations

Materials.—(i) *γ-p-Acetylphenylbutyric acid.* Ethyl γ-phenylbutyrate (30 g.) was gradually added to a mixture of aluminium chloride (90 g., 2 mol.) and acetyl chloride (25 g., 1 mol.) in ethylene chloride. When reaction was complete (15 min.) the mixture was decomposed with ice and dilute hydrochloric acid. Ethyl *γ-p*-acetylphenylbutyrate (30 g., 83%), b. p. 196—197°/12 mm., was obtained. It gave a *semicarbazone*, m. p. 188—189° (Found : C, 62·0; H, 7·4; N, 14·5. $C_{15}H_{21}O_3N_3$ requires C, 61·8; H, 7·2; N, 14·45%). Acid hydrolysis of the keto-ester gave the required *keto-acid* (22 g.) as needles, m. p. 53—54° (Found : C, 69·7; H, 6·9. $C_{12}H_{14}O_3$ requires C, 70·0; H, 6·8%). Attempts to prepare this compound by acetylation of γ-phenylbutyric acid gave α-tetralone (90%), identified by its oxime, m. p. and mixed m. p. 102—103°.

(ii) *γ-p-Carboxyphenylbutyric acid* was obtained from the above keto-acid by hypochlorite oxidation; it separated from water as needles, m. p. 194—195° (Found : C, 63·4; H, 5·8%; equiv., 101. $C_{11}H_{12}O_4$ requires C, 63·6; H, 5·8%; equiv., 104).

(iii) β-p-*Acetylphenylpropionic acid.* Methyl β-phenylpropionate (45 g.) in methylene chloride (100 ml.) was gradually added to a solution of aluminium chloride (100 g., 2·5 mol.) and acetyl chloride (100 g., 5 mol.) in methylene chloride (300 ml.). The brisk reaction gave *methyl* β-p-*acetylphenylpropionate* (52 g., 93%), b. p. 175°/12 mm. It gave a *semicarbazone*, m. p. 162—163° from methanol (Found : C, 58·9; H, 6·5; N, 15·5. $C_{13}H_{17}O_3N_3$ requires C, 59·3; H, 6·5; N, 16·0%). Acid hydrolysis of the keto-ester gave the required *keto-acid* (40 g.) which separated from water as long needles, m. p. 120° (Found : C, 68·7; H, 6·5%; equiv., 196. $C_{11}H_{12}O_3$ requires C, 68·7; H, 6·25%; equiv., 192).

(iv) Hypochlorite oxidation of the keto-acid gave β-*p*-carboxyphenylpropionic acid [6] which separated from water in needles, m. p. 284°.

(v) *γ-p-Acetylphenyl-αα-dimethylbutyric acid.* αα-Dimethyl-γ-phenylbutyric acid was obtained by Clemmensen reduction of the product of interaction of αα-dimethylsuccinic anhydride, aluminium chloride (2 mols.), and benzene (1·5 mols.) in ethylene chloride.[7] Its methyl ester (20 g.) in methylene chloride (50 c.c.) was gradually added to a solution of aluminium chloride (40 g., 3 mols.) and acetyl chloride (40 g., 5 mols.) in methylene chloride (150 c.c.). The rapid reaction gave methyl *γ-p*-acetylphenyl-αα-dimethylbutyrate (18 g.), b. p. 200°/12 mm. Its *semicarbazone* separated from methanol in needles, m. p. 193° (Found : C, 63·3; H, 7·4; N, 13·6. $C_{16}H_{23}O_3N_3$ requires C, 63·0; H, 7·5; N, 13·8%). Acid hydrolysis of the keto-ester gave the required *keto-acid* (16 g.), b. p. 196°/0·5 mm., needles (from light petroleum), m. p. 63° (Found : C, 71·4; H, 7·6. $C_{14}H_{18}O_3$ requires C, 71·7; H, 7·7%).

[6] Cf. Widman, *Ber.*, 1889, **22**, 2272.
[7] Cf. Rothstein and Saboor, *J.*, 1943, 425.

Cyclisations.—The above keto-acids and dicarboxylic acids were fused with aluminium chloride (5 mols.) and sodium chloride (1 mol.) at 180° for an hour. The reaction mixtures were decomposed with ice and hydrochloric acid and the products were isolated in the usual way.

(i) γ-*p*-Acetylphenylbutyric acid (3·6 g.) gave 7-*acetyl*-1-*tetralone* (2·5 g.) as needles, m. p. 67° (from light petroleum) (Found: C, 76·8; H, 6·4. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%). It was reduced by the Clemmensen method and catalytic dehydrogenation of the product gave 2-ethylnaphthalene (picrate, m. p. and mixed m. p. 77°).

(ii) γ-*p*-Carboxyphenylbutyric acid (1·6 g.) gave 7-*carboxy*-1-*tetralone* (0·5 g.), m. p. 216° (sealed tube), isolated by sublimation at 190—200°/0·2 mm. (Found: C, 69·5; H, 5·5%; equiv., 191. $C_{11}H_{10}O_3$ requires C, 69·4; H, 5·3%; equiv., 190). When reduced by the Clemmensen method, the product gave tetralin-6-carboxylic acid, m. p. and mixed m. p. 153°.

(iii) β-*p*-Acetylphenylpropionic acid gave 6-*acetylindan*-1-*one* which separated from light petroleum in needles, m. p. 98° (Found: C, 75·4; H, 5·70. $C_{11}H_{10}O_2$ requires C, 75·8; H, 5·75%). This compound combined with 2 : 4-dinitrophenylhydrazine (2 mol.), and the *product* separated from nitrobenzene in red needles, m. p. 310° (Found: C, 51·3; H, 3·4; N, 20·5. $C_{23}H_{18}O_8N_8$ requires C, 51·7; H, 3·4; N, 21·0%).

(iv) β-*p*-Carboxyphenylpropionic acid gave 6-*carboxyindan*-1-*one*, needles (from water), m. p. 256° (Found: C, 68·4; H, 4·2%; equiv., 178. $C_{10}H_8O_3$ requires C, 68·1; H, 4·55%; equiv., 176), and thence indane-5-carboxylic acid, m. p. and mixed m. p. 181°, by Clemmensen reduction.

(v) A mixture of γ-*p*-acetylphenyl-αα-dimethylbutyric acid (20 g.) and excess of aluminium and sodium chlorides decomposed at 140° with evolution of carbon monoxide and gave acetophenone (2 g.) (2 : 4-dinitrophenylhydrazone m. p. and mixed m. p. 237°), and 7-*acetyl*-1 : 2 : 3 : 4-*tetrahydro*-2-*methylnaphthalene* (12 g.). Its *semicarbazone* separated from ethanol in needles, m. p. 196° (Found: C, 68·7; H, 7·8; N, 16·7. $C_{14}H_{19}ON_3$ requires C, 68·6; H, 7·8; N, 17·1%), and its 2 : 4-*dinitrophenylhydrazone* from ethyl acetate in red needles, m. p. 200—202° (Found: C, 61·5; H, 5·0; N, 15·1. $C_{19}H_{20}O_4N_4$ requires C, 61·9; H, 5·4; N, 15·2%). It gave 5 : 6 : 7 : 8-*tetrahydro*-7-*methyl*-2-*naphthoic acid*, needles, m. p. 138—140° (from water) (Found: C, 75·4; H, 7·4%; equiv., 192. $C_{12}H_{14}O_2$ requires C, 75·8; H, 7·4%; equiv., 190), when oxidised with alkaline hypochlorite. This acid was decarboxylated and dehydrogenated by palladium–charcoal in quinoline and gave 2-methylnaphthalene (picrate m. p. and mixed m. p. 115°).

Intramolecular Alkylation

Preparation of Phenylalkyl Halides and their p-*Acetyl Derivatives.*—(i) 1-Chloro-4-phenylbutane,[8] b. p. 120°/15 mm., (ii) 1-chloro-3-phenylbutane,[9] b. p. 100°/13 mm., (iii) 1-chloro-2-methyl-3-phenylpropane,[10] b. p. 101°/11 mm., (iv) 2-chloro-1-phenylpropane,[11] b. p. 98°/18 mm., (v) 1-chloro-5-phenylpentane,[12] b. p. 120°/12 mm., (vi) 4-chloro-1-phenylpentane, b. p. 100°/12 mm., and (vii) 3-chloro-1-phenylpentane, b. p. 100°/12 mm., were prepared from the corresponding alcohols by the action of thionyl chloride. 2-*Benzyl*-2-*chloropropane*, b. p. 92°/13 mm. (Found: Cl, 20·8. $C_{10}H_{13}Cl$ requires Cl, 21·0%), was prepared from 2-methyl-1-phenylpropan-2-ol by the combined action of concentrated hydrochloric acid and calcium chloride.

Friedel–Crafts acetylation of the aralkyl chlorides was attempted as follows: A solution of aluminium chloride (1·0 mol. as $AlCl_3$) in a mixture of acetyl chloride (1·5 mol.) and methylene chloride was gradually added to a stirred solution of the aralkyl chloride in methylene chloride. The reaction was over in a few nimutes and the mixture was decomposed with ice and hydrochloric acid. The organic layer was separated, washed with water, dried (Na_2SO_4), and distilled.

(i) 1-p-*Acetylphenyl*-4-*chlorobutane* (75% yield), b. p. 185—190°/12 mm., gave a 2 : 4-*dinitrophenylhydrazone* which separated from ethanol in orange-red needles, m. p. 144° (Found: Cl, 9·5; N, 14·3. $C_{18}H_{19}O_4N_4Cl$ requires Cl, 9·1; N, 14·3%). This chloro-ketone was also given by the action of concentrated hydrochloric acid and zinc chloride on the corresponding hydroxy-ketone, b. p. 160°/0·5 mm. [2 : 4-*dinitrophenylhydrazone*, m. p. 89° (Found: C, 57·6; H, 5·0; N, 15·2. $C_{18}H_{20}O_5N_4$ requires C, 58·1; H, 5·4; N, 15·1%)], which was obtained by the Friedel–Crafts acetylation of 4-phenylbutyl acetate.

(ii) 1-*p*-Acetylphenyl-3-chlorobutane, b. p. 175°/15 mm., was obtained in only 12% yield.

[8] Von Braun, *Ber.*, 1910, **43**, 2846.
[9] Von Braun and Neumann, *Ber.*, 1917, **50**, 53.
[10] Von Braun, Grabowski, and Kirschbaum, *Ber.*, 1913, **46**, 1278, 3041.
[11] Huston and Sager, *J. Amer. Chem. Soc.*, 1926, **48**, 1957.
[12] Ruzicka and Peyer, *Helv. Chim. Acta*, 1935, **18**, 676.

Its *semicarbazone* separated from ethanol in needles, m. p. 174° (Found: C, 58·8; H, 7·2; N, 15·3; Cl, 12·8. $C_{13}H_{18}ON_3Cl$ requires C, 58·3; H, 6·8; N, 15·7; Cl, 13·3%).

(iii) 1-*p*-Acetylphenyl-2-methyl-3-chloropropane (84% yield), b. p. 170°/12 mm., gave a *semicarbazone* which separated from ethanol in needles, m. p. 196° (Found: C, 57·9; H, 6·8; N, 15·2; Cl, 12·8. $C_{13}H_{18}ON_3Cl$ requires C, 58·3; H, 6·8; N, 15·7; Cl, 13·3%).

(iv) Attempts to acetylate 2-chloro-1-phenylpropane gave only non-volatile material.

(v) 1-*p*-Acetylphenyl-5-chloropentane (84% yield), b. p. 188°/12 mm., gave a *semicarbazone* which separated from ethanol in needles, m. p. 156° (Found: C, 60·4; H, 6·9; N, 15·4. $C_{14}H_{20}ON_3Cl$ requires C, 60·0; H, 7·1; N, 15·0%).

(vi) 1-p-*Acetylphenyl-4-chloropentane* (65% yield), b. p. 195°/23 mm. (Found: Cl, 15·6. $C_{13}H_{17}OCl$ requires Cl, 15·8%), was hydrolysed during its interaction with semicarbazide solution; the *product* did not contain chlorine and separated from ethanol in needles, m. p. 196° (Found: C, 68·4; H, 7·6; N, 15·8. $C_{14}H_{21}O_2N_3$ requires C, 68·8; H, 8·0; N, 16·0%).

(vii) 1-p-*Acetylphenyl-3-chloropentane* (50% yield), b. p. 190°/20 mm. (Found: Cl, 15·5. $C_{13}H_{17}OCl$ requires Cl, 15·8%), gave the *semicarbazone* of the corresponding hydroxy-ketone as needles, m. p. 192°, from ethanol (Found: C, 68·4; H, 7·7; N, 16·3. $C_{14}H_{21}O_2N_3$ requires C, 68·8; H, 8·0; N, 16·0%).

Cyclisation of Phenylalkyl Chlorides.—In each instance this was effected by addition of the organic chloride to a suspension of finely powdered aluminium chloride in light petroleum (b. p. 60—80°) and boiling the mixture under reflux for an hour.

1-Chloro-3-phenylpropane, 1-chloro-4-phenylbutane and 1-chloro-5-phenylpentane gave indane, tetralin, and benzosuberane respectively in 50% yield. These hydrocarbons were identified by the semicarbazones of their acetyl derivatives. Addition of the semicarbazone of *p-cyclo*pentylacetophenone (m. p. 216°) to that of 7-acetylbenzosuberane (m. p. 209°) depresses the m. p. of the latter (cf. ref. 4). 4-Chloro-1-phenylpentane gave 1 : 2 : 3 : 4-tetrahydro-1-methylnaphthalene (40%), b. p. 95°/12 mm., n_D^{20} 1·5285, which was dehydrogenated to 1-methylnaphthalene (picrate m. p. and mixed m. p. 140°) with palladium–charcoal at 280°. 3-Chloro-1-phenylpentane gave 1-ethylindane [12] (40%), b. p. 93°/12 mm., n_D^{22} 1·5235, whose 6-acetyl derivative gave a 2 : 4-*dinitrophenylhydrazone*, m. p. and mixed m. p. 154° (Found: C, 62·3; H, 5·4; N, 15·2. $C_{19}H_{20}O_4N_4$ requires C, 61·9; H, 5·4; N, 15·2%).

Cyclisation of p-*Acetylphenylalkyl Chlorides.*—This was effected by adding the chlorides to a stirred melt of aluminium chloride (5 parts) containing sodium chloride (10%) at 100°. The mixtures were stirred for an hour, then decomposed with ice and hydrochloric acid, and the products were isolated by distillation. Yields were 60—70%.

1-*p*-Acetylphenyl-4-chlorobutane, 1-*p*-acetylphenyl-3-chlorobutane and 1-*p*-acetylphenyl-2-methyl-3-chloropropane gave 5-acetyl-2-methylindane. Its 2 : 4-*dinitrophenylhydrazone* separated from ethanol in orange-red needles, m. p. and mixed m. p. 192° (Found: C, 60·6; H, 4·9; N, 15·6. $C_{18}H_{18}O_4N_4$ requires C, 61·0; H, 5·1; N, 15·9%). Authentic 5-acetyl-2-methylindane was obtained by acetylation of 2-methylindane.[13]

Cyclisation of the 5-, 4-, and 3-chloro-derivatives of 1-*p*-acetylphenylpentane gave 5-acetyl-2-ethylindane, b. p. 165°/20 mm., in each instance. An authentic sample was obtained by acetylation of 2-ethylindane.[14] Its *semicarbazone* separated from ethanol in needles, m. p. 215° (Found: C, 68·1; H, 7·7; N, 16·9. $C_{14}H_{19}ON_3$ requires C, 68·5; H, 7·8; N, 17·2%), and its 2 : 4-*dinitrophenylhydrazone* from acetic acid in orange-red needles, m. p. 186° (Found: C, 61·5; H, 5·5; N, 14·9. $C_{19}H_{20}O_4N_4$ requires C, 61·9; H, 5·5; N, 15·2%).

Preparation and Cyclisation of Bromoalkyl Phenyl Ketones.—(i) γ-Bromobutyrophenone (60 g.), b. p. 155—160°/15 mm., was obtained by adding a solution of γ-bromobutyryl chloride (80 g.) and aluminium chloride (60 g.) in methylene chloride (150 c.c.) to benzene (70 g., 2 mols.). It separated from light petroleum (b. p. 40°) in large plates m. p. 38—38·5° (Found: C, 53·1; H, 4·6; Br, 34·9. $C_{10}H_{11}OBr$ requires C, 52·8; H, 4·85; Br, 35·2%), and gave a 2 : 4-*dinitrophenylhydrazone* which separated from ethyl acetate in orange-red needles, m. p. 161° (Found: C, 47·5; H, 3·7; N, 13·4; Br, 19·3. $C_{16}H_{15}O_4N_4Br$ requires C, 47·1; H, 3·68; N, 13·75; Br, 19·65%).

(ii) *γ-Bromovalerophenone*, b. p. 150°/10 mm., was similarly prepared from γ-bromovaleryl chloride, as needles (from light petroleum), m. p. 26° (Found: C, 54·5; H, 5·5; Br, 32·7. $C_{11}H_{13}OBr$ requires C, 54·7; H, 5·4; Br, 33·2%). The 2 : 4-*dinitrophenylhydrazone* separated from ethyl acetate in yellow-orange needles, m. p. 166—168° (Found: C, 48·7; H, 4·3; N, 13·5; Br, 18·5. $C_{17}H_{17}O_4N_4Br$ requires C, 48·5; H, 4·0; N, 13·3; Br, 19·0%).

[13] Plattner and Wyss, *Helv. Chim. Acta.*, 1941, **24**, 483.
[14] Wagner and Jauregg, *Ber.*, 1941, **74**, 1522.

The bromoalkyl phenyl ketones (10 g.) were cyclised by aluminium chloride (30 g.) and sodium chloride (4 g.) at 100° for an hour.

(i) γ-Bromobutyrophenone gave 3-methylindan-1-one [10] (4 g.), b. p. 120°/8 mm., identified by its semicarbazone, m. p. and mixed m. p. 230°, and by its 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 240°.[15]

(ii) γ-Bromovalerophenone gave 4-methyl-1-tetralone (5 g.), b. p. 120—125°/8 mm., identified by its semicarbazone,[16] m. p. and mixed m. p. 210°, and by its 2 : 4-*dinitrophenylhydrazone*, orange plates, m.p. and mixed m. p. 216—217° (from ethyl acetate) (Found : C, 60·0; H, 4·8; N, 16·8. $C_{17}H_{16}O_4N_4$ requires C, 60·0; H, 4·7; N, 16·5%).

Fusion of β-Benzoyl-αα-dimethylpropionic Acid with Excess of Aluminium Chloride.—The keto-acid (10 g.) was gradually added to a stirred melt of aluminium chloride (30 g.) and sodium chloride (3 g.) at 140°. After an hour at 140° the mixture afforded initial keto-acid (3 g.) and 3 : 3-dimethylindan-1-one (4 g., 60%), b. p. 115—117°/18 mm. Its semicarbazone [17] separated from ethanol in needles, m. p. 205—207° (Found : C, 66·1; H, 6·7; N, 19·0. Calc. for $C_{12}H_{15}ON_3$: C, 66·4; H, 6·9; N, 19·3%), and its 2 : 4-*dinitrophenylhydrazone* from ethyl acetate in red needles, m. p. 266° (Found : C, 60·1; H, 4·6; N, 16·0. $C_{17}H_{16}O_4N_4$ requires C, 60·0; H, 4·7; N, 16·5%). Clemmensen reduction of the ketone gave 1 : 1-dimethylindane which was identified as the 2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 212°, of its 6-acetyl derivative.

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[15] Marvel, Dee, and Cooke, *J. Amer. Chem. Soc.*, 1940, **62**, 3499, 3503.
[16] Meyer and Stamm, *Ber.*, 1923, **56**, 1424.
[17] Von Auwers, *Ber.*, 1921, **54**, 994.