506. *Cinnolines. Part XXII. Experiments in the Indane and Tetralin Series. Some New 4-Hydroxycinnolines.*

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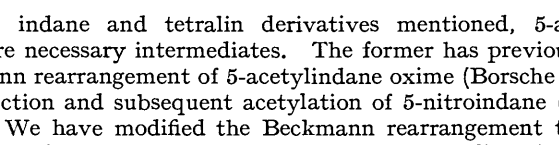
The synthesis of some 4-hydroxy*cyclo*penteno- and 4-hydroxy*cyclo*hexeno-cinnolines from indane and tetralin derivatives is described. Some 4-hydroxy-*Bz*-methylcinnolines are also mentioned.

The aims of the present work were three-fold: first, to utilise several known ω-chloro-*o*-amino-acetophenones in extending the synthesis of 3-halogeno-4-hydroxycinnolines previously described (Schofield and Simpson, Part XVIII, *J.*, 1948, 1170); secondly, to examine any effect upon the synthesis which a five- or six-membered ring fused to the aromatic ring of the acetophenone might have; and thirdly, to provide intermediates which might lead eventually to the synthesis of benzocinnolines.

Four ketones useful for our purpose have been described in the literature, namely, ω-chloro-2-acetamido-5-methyl- (I; R = Cl, R′ = Me, R″ = H) (Kunckell, *Ber.*, 1900, **33**, 2644) and ω-chloro-2-acetamido-4 : 5-dimethyl-acetophenone (I; R = Cl; R′ = R″ = Me) (Kunckell and Schneider, *J. pr. Chem.*, 1912, **86**, 430), also 5-acetamido-6-chloroacetylindane (I; R = Cl, R′R″ = $[CH_2]_3$) and 6-acetamido-7-chloroacetyltetralin (III) (Kranzlein, *Ber.*, 1937, **70**, 1776).



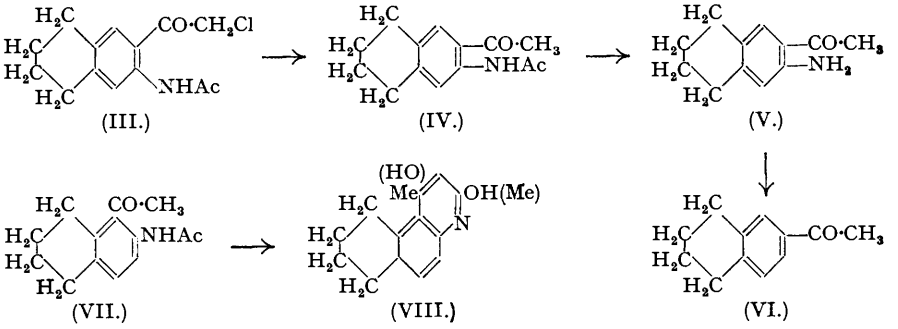
(I.) (II.)

In preparing the indane and tetralin derivatives mentioned, 5-acetamidoindane and 6-acetamidotetralin are necessary intermediates. The former has previously been obtained in poor yield by Beckmann rearrangement of 5-acetylindane oxime (Borsche and John, *Ber.*, 1924, **57**, 656), and by reduction and subsequent acetylation of 5-nitroindane (Lindner and Bruhin, *Ber.*, 1927, **60**, 435). We have modified the Beckmann rearrangement to give high yields of 5-acetamidoindane. Similarly, the rearrangement of 6-acetyltetralin oxime provides a practical route to 6-acetamidotetralin. The subsequent Friedel–Crafts reactions have been improved.

The monomethyl- (I; R = Cl, R′ = Me, R″ = H), dimethyl- (I; R = Cl, R′ = R″ = Me), and tetralin-compounds (III) were hydrolysed, and the resulting amines diazotised without isolation, giving good yields of 3-*chloro*-4-*hydroxy*-6-*methyl*- (II; R = Cl, R′ = Me, R″ = H), 3-*chloro*-4-*hydroxy*-6 : 7-*dimethyl*- (II; R = Cl, R′ = R″ = Me), and 3-*chloro*-4-*hydroxy*-6 : 7-cyclo*hexeno-cinnoline* (II; R = Cl, R′R″ = $[CH_2]_4$), respectively. In contrast to this, numerous experiments with (I; R = Cl, R′R″ = $[CH_2]_3$) failed, until it emerged that successful cinnoline formation in this case was dependent on the use of concentrated acid media and avoidance of excess of nitrous acid; in these circumstances a high yield of 3-*chloro*-4-*hydroxy*-6 : 7-cyclo*pentenocinnoline* resulted.

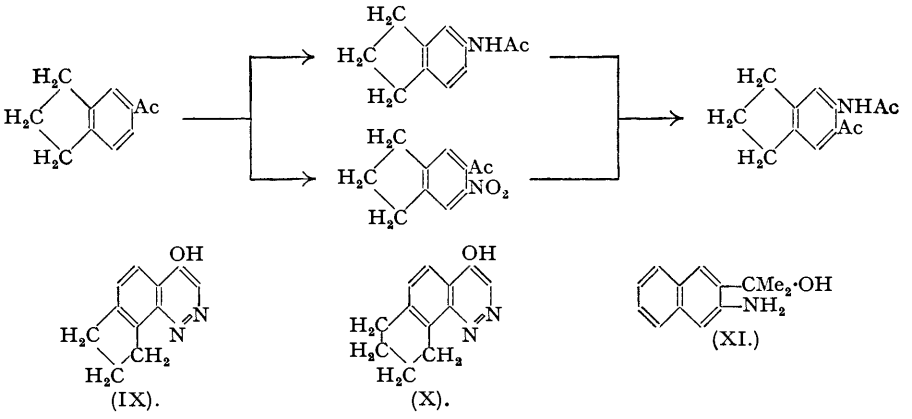
These observations made it of interest to determine if difficulties were presented to cinnoline formation by indane compounds in general. 5-*Acetamido*-6-*acetylindane* (I; R = H, R′R″ = $[CH_2]_3$) was prepared by Friedel–Crafts acetylation of 5-acetamidoindane. The derived 5-*amino*-6-*acetylindane* readily provided 4-*hydroxy*-6 : 7-cyclo*pentenocinnoline* (II; R = H, R′R″ = $[CH_2]_3$) on diazotisation, showing that the difficulty in the former case is peculiar to the chloroacetyl compound. That Friedel–Crafts acylation of 5-acetamidoindane pro-

ceeds in the same sense with both acetyl and chloroacetyl chlorides, was proved by dehalogenation of the product (I; R = Cl, R′R″ = $[CH_2]_3$) from the latter reaction, which gave 5-acetamido-6-acetylindane, identical with the compound from the Friedel–Crafts reaction employing acetyl chloride. Similar dehalogenation of the tetralin derivative (III) gave 6-*acetamido*-7-*acetyltetralin* (IV), whence was derived 6-*amino*-7-*acetyltetralin* (V), and likewise (I; R = Cl, R′ = R″ = Me) provided 2-*amino*-4 : 5-*dimethylacetophenone*. Diazotisation of these amines gave 4-*hydroxy*-6 : 7-cyclo*hexeno*- (II; R = H, R′R″ = $[CH_2]_4$) and 4-*hydroxy*-6 : 7-*dimethyl-cinnoline*. Hoping to prepare 6-acetamido-7-acetyltetralin more directly, we examined the Friedel–Crafts acetylation of 6-acetamidotetralin, but the *acetamido-ketone*, m. p. 107—108°, obtained proved to be different from the compound (m.p. 119—119·5°) described above. In view of this it became necessary to confirm the assumed structure (IV) of the latter, and this was easily effected



in the steps (III) ⟶ (VI), 6-acetyltetralin being identified as its oxime. Evidently then, Friedel–Crafts acetylation of 6-acetamidotetralin proceeds in a different sense from the corresponding chloroacetylation. From the product of the acetylation, m. p. 107—108°, we were unable to obtain a free amine by either alkaline or acid hydrolysis. Both reactions proved complicated, but from the latter a *compound*, m. p. 282—283°, apparently (VIII), was isolated and, if this representation of its structure is correct, the Friedel–Crafts product is clearly 6-*acetamido*-5-*acetyltetralin* (VII).

To obtain other indane and tetralin derivatives suitable for cinnoline syntheses, the nitration of 5-acetylindane and of 6-acetyltetralin was examined. The former compound was first nitrated by Borsche and John (*loc. cit.*), who obtained a product said to be 4-nitro-5-acetylindane, evidence for this structure being based on the formation from the compound, by standard reactions, of a substance held to be 4-aminoindane. This work is invalidated by a later paper (*Ber.*, 1926, **59**, 1909) in which Borsche showed that the former product was a mixture of two, or possibly three, compounds from which he isolated a small yield of a substance, m. p. 82°, still presumed to be 4-nitro-5-acetylindane. Lindner and Bruhin (*loc. cit.*), who prepared authentic 4-aminoindane, expressed doubt as to the nature of the material assigned this



structure by Borsche and John (*loc. cit.*). On repeating the nitration of 5-acetylindane, using the conditions described by the earlier workers, we isolated 5-nitro-6-acetylindane,

m. p. 82—83°, which on reduction gave 5-amino-6-acetylindane, identical with the compound already described above. The sequence of reactions involved, illustrated below, confirms the orientation of the products in question, both from the Friedel–Crafts reaction and the nitration. A second *isomer*, m. p. 91°, was also isolated from the nitration product of 5-acetylindane, and is proved to be 4-*nitro*-5-*acetylindane* by the fact that the derived *amine* yielded 4-*hydroxy*-7 : 8-cyclo*pentenocinnoline* (IX) on diazotisation. Borsche and Bodenstein (*Ber.*, 1926, **59**, 1915) obtained 5-nitro-6-acetyltetralin in poor yield from the nitration of 6-acetyltetralin. The structure of this compound is confirmed by the formation from the related *amine* of 4-*hydroxy*-7 : 8-cyclo*hexenocinnoline* (X).

The 6 : 7-*cyclo*hexenocinnoline derivatives described above are being examined as possible sources of 6 : 7-benzocinnolines.

Obviously, suitably substituted naphthalene derivatives would offer the most direct route to the synthesis of benzocinnolines. Hoping to form the 5 : 6-benzcinnoline ring system Leonard and Boyd (*J. Org. Chem.*, 1946, **11**, 419) diazotised what they believed to be 2-amino-1-acetylnaphthalene, but later (Leonard and Hyson, *ibid.*, 1948, **13**, 164) it was shown that the amine did not possess this structure. Realising the promoting effect of a ω-halogen atom upon cinnoline formation from *o*-aminoacetophenones, we investigated the Friedel–Crafts reaction between β-acetonaphthalide and chloroacetyl chloride. Two isomeric *acetamidochloroacetylnaphthalenes*, m. p. 220—221° and 158·5—159°, respectively, were isolated. The former was shown to be 2-*acetamido*-6-*chloroacetylnaphthalene* by dehalogenation to 6-*acetamido*-2-*acetonaphthone*, which was hydrolysed and converted by a Sandmeyer reaction into 6-chloro-2-acetonaphthone. This gave, in a Schmidt reaction, 6-chloro-2-acetamidonaphthalene, m. p. 182—183°, apparently identical (mixed m. p. determination) with an authentic specimen (Clemo and Legg, *J.*, 1947, 545). Hydrolysis of 2-acetamido-6-chloroacetylnaphthalene, and diazotisation in hydrochloric acid, gave a mixture of 2-*hydroxy*-6-*chloroacetylnaphthalene* and 2-*chloro*-6-*chloroacetylnaphthalene*. The latter product was also formed by treating the diazonium solution with cuprous chloride. The orientation of the lower-melting product from the Friedel–Crafts reaction has not yet been completed, but it gave on hydrolysis and diazotisation *hydroxychloroacetylnaphthalene*, m. p. 143—144°, in low yield, which seems to indicate that the acetamido-compound is not a 1 : 2-substituted naphthalene derivative.

A more promising route to the 6 : 7-benzocinnoline nucleus would appear to be offered through 2-*amino*-3-*naphthyldimethylcarbinol* (XI), which we hope to dehydrate to the related ethylene and convert thence into the cinnoline by diazotisation. The carbinol was prepared by a Grignard reaction upon methyl 3-amino-2-naphthoate.

Experimental.

M.p.s are uncorrected. Unless otherwise stated, all extracts were dried with sodium sulphate, and all diazotisations were effected at 0—5°.

ω-*Chloro*-2-*acetamido*-5-*methylacetophenone*.—By Kunckell's method (*loc. cit.*) *p*-acetotoluidide (15 g.) gave 19·5 g. of crude mixed isomers. The combined products of two such experiments gave, by fractional crystallisation from ethanol, 3·01 g. of the required compound, m. p. 177—179°.

ω-*Chloro*-2-*acetamido*-4 : 5-*dimethylacetophenone*.—Under the conditions of Kunckell and Schneider (*loc. cit.*) aceto-3 : 4-xylidide (10 g.) gave 10·7 g. of pure product as pink needles, m. p. 166—167°.

5-*Acetamidoindane*.—A solution of 5-acetylindane oxime (5·9 g.; Borsche and Pommer, *Ber.*, 1921, **54**, 102) in acetic anhydride (5 c.c.) and acetic acid (10 c.c.) was saturated with hydrogen chloride and set aside for 24 hours, and the precipitate (5 g., 85%), m. p. 105—106°, collected.

6-*Acetamidotetralin*.—6-Acetyltetralin (10 g.) (prepared in 82% yield by the method of Scharwin, *Ber.*, 1902, **35**, 2511) provided the oxime (7·0 g.), m. p. 105—106°. This, treated as above in acetic anhydride (10 c.c.) and acetic acid (20 c.c.), gave 6-acetamidotetralin (4·2 g., 60%), m. p. 105—106°.

5-*Acetamido*-6-*chloroacetylindane*.—By Kränzlein's method (*loc. cit.*) 5-acetamidoindane (5 g.) gave the chloro-ketone (1·6 g.), m. p. 165—166°.

6-*Acetamido*-7-*chloroacetyltetralin*.—6-Acetamidotetralin (16 g.), carbon disulphide (60 c.c.), and chloroacetyl chloride (40 c.c.) were stirred at 0°, powdered aluminium chloride (40 g.) was added during ½ hour, and the whole stirred for 2 hours at room temperature. The solvent was decanted, the complex decomposed with ice and hydrochloric acid, and the product extracted with chloroform. Removal of the chloroform and crystallisation of the residue (10 g.) from alcohol gave the product (7·5 g.), m. p. 147—148°. Kränzlein's method never gave more than 10% yields.

3-*Chloro*-4-*hydroxy*-6-*methylcinnoline*.—The acetamido-compound (2·3 g.) and acetic acid–20% hydrochloric acid (46 c.c.; 1 : 1) were heated at 95° for 1 hour, and the solution was cooled to 5—10° (lower temperatures precipitated the difficultly soluble hydrochloride) and diazotised with aqueous sodium nitrite (5%). After 1 week at room temperature and ½ hour at 75°, the substantially pure product was collected (1·72 g.). 3-*Chloro*-4-*hydroxy*-6-*methylcinnoline* formed soft white needles, m. p. 298·5—299·5°, from alcohol (Found : C, 55·3; H, 3·7; N, 14·3. $C_9H_7ON_2Cl$ requires C, 55·5; H, 3·6; N, 14·4%). The *acetyl* derivative formed white needles, m. p. 186—187°, from the same solvent (Found : C, 55·7; H, 3·7. $C_{11}H_9O_2N_2Cl$ requires C, 55·8; H, 3·8%).

3-*Chloro*-4-*hydroxy*-6 : 7-*dimethylcinnoline*.—The relevant acetamido-compound (0·5 g.), by the same method as that above, gave 3-*chloro*-4-*hydroxy*-6 : 7-*dimethylcinnoline* (0·37 g.) as colourless needles, m. p. (310) 314—315°, from alcohol (Found: C, 57·1; H, 4·5. $C_{10}H_9ON_2Cl$ requires C, 57·5; H, 4·3%). From alcohol the *acetyl* derivative gave silky needles, m. p. 196—197° (Found: C, 57·3; H, 4·2. $C_{12}H_{11}O_2N_2Cl$ requires C, 57·7; H, 4·0%).

3-*Chloro*-4-*hydroxy*-6 : 7-cyclo*pentenocinnoline*.—5-Acetamido-6-chloroacetylindane (0·2 g.), concentrated hydrochloric acid (5 c.c.), and acetic acid (5 c.c.) were heated for ½ hour at 95°, the solution was diazotised with sodium nitrite (0·1 g.) in water (1 c.c.), concentrated hydrochloric acid (20 c.c.) added, and the whole heated at 95° until coupling with alkaline β-naphthol no longer occurred. The residue remaining after neutralisation of the solution with sodium acetate, and evaporation, was triturated with water and then crystallised from alcohol. Further crystallisation of the product (0·1 g.) from this solvent gave colourless leaflets of 3-*chloro*-4-*hydroxy*-6 : 7-cyclo*pentenocinnoline*, m. p. >340° (Found: C, 59·9; H, 4·3; N, 12·7. $C_{11}H_9ON_2Cl$ requires C, 59·9; H, 4·1; N, 12·7%). The *acetyl* derivative gave colourless needles, m. p. 159—160°, from dilute alcohol (Found: C, 59·6; H, 4·1. $C_{13}H_{11}O_2N_2Cl$ requires C, 59·4; H, 4·2%).

3-*Chloro*-4-*hydroxy*-6 : 7-cyclo*hexenocinnoline*.—A solution prepared by hydrolysing 6-acetamido-7-chloroacetyltetralin (0·1 g.) with hydrochloric acid (5 c.c.; 20%), and diazotising as in the case of the monomethyl compound above, gave a fawn-coloured solid (0·06 g.), which formed colourless crystals of 3-*chloro*-4-*hydroxy*-6 : 7-cyclo*hexenocinnoline*, m. p. 288—289°, from alcohol (Found: C, 61·4; H, 4·7. $C_{12}H_{11}ON_2Cl$ requires C, 61·4; H, 4·7%). The *acetyl* derivative formed colourless needles, m. p. 148—149°, from ethanol (Found: C, 60·3; H, 4·7. $C_{14}H_{13}O_2N_2Cl$ requires C, 60·8; H, 4·7%).

5-*Acetamido*-6-*acetylindane*.—Aluminium chloride (6 g.) was added during 10 minutes to a stirred mixture of 5-acetamidoindane (3·5 g.), carbon disulphide (30 c.c.), and acetyl chloride (1·7 c.c.), cooled in water, the whole stirred for ½ hour more, the solvent decanted, and the complex decomposed with ice and hydrochloric acid. Extraction with chloroform, removal of the solvent, and crystallisation of the residue from alcohol gave a product (1·25 g.), m. p. 115—116°. Pure 5-*acetamido*-6-*acetylindane* formed white prisms, m. p. 119—120°, from alcohol (Found: C, 72·2; H, 7·1. $C_{13}H_{15}O_2N$ requires C, 71·9; H, 6·9%).

5-*Amino*-6-*acetylindane*.—(i) The acetamido-compound (0·5 g.) and hydrochloric acid (10 c.c.; 20%) were heated under reflux for ½ hour, the solution made alkaline, and the product collected (0·42 g.). 5-*Amino*-6-*acetylindane* gave pale yellow needles, m. p. 131·5—132·5°, from dilute alcohol (Found: C, 75·5; H, 7·5. $C_{11}H_{13}ON$ requires C, 75·4; H, 7·4%).

(ii) 5-Acetamido-6-chloroacetylindane (0·2 g.) was hydrolysed as in (i) above, and the amine hydrochloride which separated [m. p. 214° (decomp.)] decomposed with aqueous ammonium carbonate, giving the free base (0·13 g.), m. p. 137—139°. The base (0·5 g.), alcohol (20 c.c.), and zinc dust (2 g.; etched with dilute sulphuric acid and washed with water) were boiled under reflux for ½ hour, the mixture was filtered, the zinc was washed with ether, and the combined filtrate and washings were diluted and extracted with ether. Removal of the solvent and crystallisation of the residue from dilute alcohol gave 5-amino-6-acetylindane (0·25 g.), m. p. 130—131°, identical with that above.

4-*Hydroxy*-6 : 7-cyclo*pentenocinnoline*.—The hydrochloride suspension from 5-amino-6-acetylindane (0·5 g.) and concentrated hydrochloric acid (25 c.c.) was diazotised with sodium nitrite (0·5 g.) in water (2 c.c.). Concentrated hydrochloric acid (100 c.c.) was added, the solution heated for ½ hour at 95°, and worked up as in the case of the analogous 3-chloro-compound, giving a fawn-coloured solid (0·32 g.). 4-*Hydroxy*-6 : 7-cyclo*pentenocinnoline* separated from alcohol in colourless prisms, m. p. 271—272° (Found: C, 70·15; H, 5·2. $C_{11}H_{10}ON_2$ requires C, 71·0; H, 5·05%). The *acetyl* derivative formed pinkish needles, m. p. 112—113°, from dilute alcohol (Found: C, 67·9; H, 5·2. $C_{13}H_{12}O_2N_2$ requires C, 68·4; H, 5·3%).

6-*Acetamido*-7-*acetyltetralin*.—6-Acetamido-7-chloroacetyltetralin (10 g.), etched zinc (100 g.), and alcohol (100 c.c.) were boiled under reflux and stirred vigorously for 8 hours, and the mixture was poured into water and extracted with ether. Removal of the solvent gave the product (8·42 g.), m. p. 118—120°. Crystallisation from dilute methanol gave white needles of 6-*acetamido*-7-*acetyltetralin*, m. p. 119—119·5° (Found: C, 72·9; H, 7·4. $C_{14}H_{17}O_2N$ requires C, 72·7; H, 7·4%).

6-*Amino*-7-*acetyltetralin*.—The acetamido-compound (6 g.) and hydrochloric acid (200 c.c.; 50%) were boiled under reflux for 1 hour, the solution was made alkaline, and the substantially pure product (4·8 g.) crystallised from dilute methanol, giving lemon needles of 6-*amino*-7-*acetyltetralin*, m. p. 118·5—119° (Found: C, 75·4; H, 7·8. $C_{12}H_{15}ON$ requires C, 76·1; H, 8·0%).

In one experiment the solution obtained from the acetamido-compound (1 g.) by hydrolysis was diazotised with sodium nitrite (0·3 g.) in water (5 c.c.), treated with hypophosphorous acid (7 c.c.; 30%), and kept overnight at 0°. Basification and ether extraction gave an oil (0·32 g.), which, from aqueous alcohol, formed an oxime, m. p. 102—104°, alone and mixed with authentic 6-acetyltetralin oxime.

4-*Hydroxy*-6 : 7-cyclo*hexenocinnoline*.—6-Amino-7-acetyltetralin (4 g.) was diazotised in concentrated hydrochloric acid (500 c.c.) with aqueous sodium nitrite (5%), the solution left for 3 days at room temperature and worked up as described for 3-chloro-4-hydroxy-6 : 7-*cyclo*pentenocinnoline. The practically pure product (2·95 g.) formed, from methanol, small white rhombs of 4-*hydroxy*-6 : 7-cyclo*hexenocinnoline*, m. p. 262—263° (Found: C, 71·6; H, 6·1. $C_{12}H_{12}ON_2$ requires C, 71·9; H, 6·0%).

2-*Amino*-4 : 5-*dimethylacetophenone*.—ω-Chloro-2-acetamido-4 : 5-dimethylacetophenone (1 g.), concentrated hydrochloric acid, water, and acetic acid (10 c.c. of each) were heated for ½ hour at 95°, the solution was made alkaline with ammonium carbonate, and the resulting free amine (0·89 g., m. p. 128—130°) heated under reflux for 2 hours with alcohol (30 c.c.) and etched zinc (5 g.). Worked up as in previous cases this gave a product (0·58 g.) forming cream-coloured needles of 2-*amino*-4 : 5-*dimethylacetophenone*, m. p. 125—126°, from dilute ethanol (Found: C, 74·0; H, 8·2. $C_{10}H_{15}ON$ requires C, 73·6; H, 8·0%).

4-*Hydroxy*-6 : 7-*dimethylcinnoline*.—The amine (0·2 g.) was diazotised with aqueous sodium nitrite (10%) in concentrated hydrochloric acid (5 c.c.), more ice-cold acid (20 c.c.) added, and the solution set aside for 2 days. Worked up as usual this gave the desired product (0·16 g.). 4-*Hydroxy*-6 : 7-*dimethyl*-

cinnoline formed buff-coloured rhombs, m. p. 267—268°, from ethanol (Found: C, 68·55; H, 5·9. $C_{10}H_{10}ON_2$ requires C, 68·95; H, 5·8%). The *acetyl* derivative yielded, from dilute ethanol, fawn leaflets, m. p. 151—152° (Found: C, 66·6; H, 6·3. $C_{12}H_{12}O_2N_2$ requires C, 66·65; H, 5·6%).

Friedel–Crafts Reaction between Acetyl Chloride and 6-Acetamidotetralin.—6-Acetamidotetralin (5 g.), acetyl chloride (25 c.c.), and carbon disulphide (15 c.c.) were stirred together and treated with aluminium chloride (25 g.) during 10 minutes at 15°. After being boiled under reflux for 2 hours the mixture was decomposed with ice, the carbon disulphide removed by distillation, and the residue extracted with ether. The extract was washed with aqueous sodium hydroxide, the solvent removed, and the residue dried on a porous plate (3·59 g.; m. p. 95—100°). Crystallisation from dilute methanol gave pink leaflets of 6-*acetamido*-5-*acetyltetralin*, m. p. 107—108° (Found: C, 70·2; H, 6·4; N, 4·8. $C_{14}H_{17}O_2N,\frac{1}{2}H_2O$ requires C, 70·0; H, 7·6; N, 5·8%).

The acetamido-compound (0·2 g.) and 2N-hydrochloric acid (5 c.c.) were heated under reflux for 10 minutes, the white needles which separated on cooling collected (0·16 g.) and crystallised from dilute acetic acid. 2(or 4)-*Hydroxy*-4(or 2)-*methyl*-5 : 6-cyclo*hexenoquinoline* formed fluffy white needles, m. p. 282—283° (Found: C, 77·5; H, 7·1; N, 6·7. $C_{14}H_{15}ON,\frac{1}{2}H_2O$ requires C, 77·2; H, 7·0; N, 6·4%). Basification of the acid hydrolysis liquor gave the *isomer*, separating from dilute methanol in lustreless white filaments, m. p. 250—251° (Found: C, 75·0; H, 6·9; N, 5·9. $C_{14}H_{15}ON,\frac{1}{2}H_2O$ requires C, 75·65; H, 7·3; N, 6·3%).

Nitration of 5-Acetylindane.—5-Acetylindane (10 g.), nitrated by the method of Borsche and John (*loc. cit.*), gave 10 g. of oily product which was boiled with alcohol (40 c.c.) for 3 hours (charcoal) (*cf.* Borsche and John) and then filtered; the solution was allowed to crystallise, giving a solid (1·5 g.), m. p. 73—75°. Recrystallisation from alcohol gave 5-nitro-6-acetylindane (1·0 g.) in colourless needles, m. p. 82—83°. The original alcoholic liquor on concentration to 30 c.c. deposited large prisms (0·75 g.), m. p. 90—91°. Crystallisation from alcohol gave fawn-coloured prisms of 4-*nitro*-5-*acetylindane*, m. p. 91—92° (Found: C, 64·4; H, 5·7. $C_{11}H_{11}O_3N$ requires C, 64·4; H, 5·4%).

5-Nitro-6-acetylindane (0·5 g.), concentrated hydrochloric acid (5 c.c.), acetic acid (1 c.c.), and stannous chloride (1·65 g.) were heated for 1 hour at 95°, and the mixture was made alkaline with aqueous sodium hydroxide and extracted with ether. The extract contained a product (0·45 g.) which crystallised from dilute alcohol in pale yellow needles, m. p. 131—132°, alone and mixed with 5-amino-6-acetylindane described above.

4-Nitro-5-acetylindane (0·75 g.) reduced as above, gave the amine (0·52 g.). 4-*Amino*-5-*acetylindane* formed colourless leaflets, m. p. 88—89°, from dilute alcohol (Found: C, 74·0; H, 7·05. $C_{11}H_{13}ON,\frac{1}{4}H_2O$ requires C, 73·5; H, 7·6%).

4-*Hydroxy*-7 : 8-cyclo*pentenocinnoline*.—The foregoing amine (0·1 g.) in concentrated hydrochloric acid (5 c.c.) was diazotised with sodium nitrite (0·05 g.) in water (1 c.c.), concentrated hydrochloric acid (20 c.c.) added, and the solution heated at 95° until it no longer coupled with alkaline β-naphthol. Worked up as in similar cases above, the mixture gave the crude product in low yield (0·02 g.). From dilute alcohol 4-*hydroxy*-7 : 8-cyclo*pentenocinnoline* formed colourless needles, m. p. 246—247° (Found: C, 70·3; H, 5·2. $C_{11}H_{10}ON_2$ requires C, 71·0; H, 5·05%).

4-*Hydroxy*-7 : 8-cyclo*hexenocinnoline*.—6-Acetyltetralin (6 g.) and concentrated sulphuric acid (60 c.c.) were stirred rapidly at −5° and treated dropwise during ½ hour with nitric acid (4 c.c.; *d* 1·5) in concentrated sulphuric acid (10 c.c.). The mixture was stirred for a further 1½ hours at −5°, poured on ice, and extracted with ether. Concentration of the extract gave white needles (1·20 g., 17%), m. p. 129—130°. Purification by crystallisation was not satisfactory, and finally the product from two such experiments was dissolved in benzene and passed over an alumina column, a small amount of 5-nitro-6-acetyltetralin (1·06 g.), m. p. 142—143°, being isolated in this manner.

A mixture of the nitro-compound (0·4 g.), concentrated hydrochloric acid (10 c.c.), and acetic acid (10 c.c.) was treated with stannous chloride (2 g.) in concentrated hydrochloric acid (2 c.c.), and the whole heated for 2 hours at 95°. On basification the solution yielded to ether a yellow solid (0·32 g.), which crystallised from dilute methanol in stout pale brown leaflets of 5-*amino*-6-*acetyltetralin*, m. p. 87—88° (Found: C, 75·9; H, 8·0. $C_{12}H_{15}ON$ requires C, 76·1; H, 8·0%).

The amine (0·32 g.) in concentrated hydrochloric acid (80 c.c.) was diazotised with aqueous sodium nitrite (10%), the mixture set aside for 3 days at room temperature, and then worked up as usual. The almost pure product (0·15 g.) gave pale buff micro-crystals of 4-*hydroxy*-7 : 8-cyclo*hexenocinnoline*, m. p. 276—277°, on crystallisation from dilute methanol (Found: C, 65·2; H, 5·8. $C_{12}H_{12}ON_2,H_2O$ requires C, 66·0; H, 6·5%).

Chloroacetylation of β-Acetonaphthalide.—β-Acetonaphthalide (18·5 g.), aluminium chloride (29·4 g.), and carbon disulphide (370 c.c.) were stirred together at 0° and treated with chloroacetyl chloride (11·3 g.) during 20 minutes. The mixture was stirred for a further ½ hour at 0° and 9 hours at room temperature, set aside overnight (14 hours), and finally stirred and boiled under reflux for 1 hour. The solvent was decanted, and the residue decomposed with ice, and, after 24 hours, collected and dried (23 g.). Crystallisation from ethanol gave a less soluble fraction (4·5 g.), m. p. 210—212°, and a more soluble fraction (5·0 g.), m. p. 147—152°. Recrystallised from ethanol, these gave, respectively, fawn-coloured needles of 2-*acetamido*-6-*chloroacetylnaphthalene*, m. p. 220—221° (Found: C, 63·75; H, 4·6; Cl, 12·9. $C_{14}H_{12}O_2NCl$ requires C, 64·25; H, 4·6; Cl, 13·5%), and dull yellow rosettes of 2-*acetamido*-x-*chloroacetylnaphthalene*, m. p. 158·5—159·5° (Found: C, 63·95; H, 4·8; Cl, 14·0%).

6-*Acetamido*-2-*acetonaphthone*.—The chloro-ketone (5 g.), alcohol (150 c.c.), and etched zinc (50 g.) were boiled under reflux and stirred for 9 hours, the mixture was filtered, the zinc was washed with ethanol, and the combined filtrate and washings were concentrated, yielding a crystalline product (3·44 g.). 6-*Acetamido*-2-*acetonaphthone* separated as stout white leaflets, m. p. 190—191°, from alcohol (Found: C, 74·0; H, 6·4. $C_{14}H_{13}O_2N$ requires C, 73·7; H, 5·7%).

6-*Chloro*-2-*acetonaphthone*.—The acetamido-compound (3 g.), hydrochloric acid (30 c.c.; 4N.), and acetic acid (30 c.c.) were heated for 1 hour at 95°, and the solution was cooled, diazotised with aqueous sodium nitrite (30%), and added to cuprous chloride (from 3·96 g. of copper sulphate) in concentrated hydrochloric acid (15 c.c.). After the mixture had been kept overnight at 0° the product was collected

(2·21 g.) and crystallised from dilute methanol, giving fluffy, pale buff needles of 6-chloro-2-acetonaphthone, m. p. 80—81° (Found: C, 70·1; H, 4·8. Calc. for $C_{12}H_9OCl$: C, 70·4; H, 4·4%) (Jacobs *et al.*, *J. Org. Chem.*, 1946, **11**, 27, give m. p. 83·5—84°).

2-*Chloro*-6-*acetamidonaphthalene*.—The ketone (0·2 g.), trichloroacetic acid (2 g.), and sodium azide (0·1 g.) were heated at 60° for 4 hours, and the mixture was diluted with water and treated with an excess of aqueous ammonia. The product was collected and crystallised from dilute ethanol, giving white needles of 2-chloro-6-acetamidonaphthalene, m. p. 182—183°, which did not depress the m. p. (183—184°) of an authentic specimen (Clemo and Legg, *loc. cit.*).

2-*Hydroxy*-6-*chloroacetylnaphthalene*.—2-Acetamido-6-chloroacetylnaphthalene (5 g.), hydrochloric acid (70 c.c.; 20%), and acetic acid (70 c.c.) were heated for 1¼ hours at 95°, and the solution was diazotised with aqueous sodium nitrite (10%) and heated for ¾ hour at 70°. Crystallisation of the product (3·62 g.) from ethanol gave a less soluble fraction (0·9 g.), m. p. 144—145°, and a more soluble one (1·77 g.), m. p. 173—177°. The first provided pale yellow needles of 2-*chloro*-6-*chloroacetylnaphthalene*, m. p. 153—154° (Found: C, 60·4; H, 3·6; Cl, 28·9. $C_{12}H_8OCl_2$ requires C, 60·3; H, 3·4; Cl, 29·7%), from alcohol, and the second gave pale buff needles of 2-*hydroxy*-6-*chloroacetylnaphthalene*, m. p. 180—181° (Found: C, 64·5; H, 4·0; Cl, 16·3. $C_{12}H_9O_2Cl$ requires C, 65·3; H, 4·1; Cl, 16·1%), from benzene. 2-Chloro-6-chloroacetylnaphthalene was also prepared by treating the diazonium solution with cuprous chloride, as above.

2-*Hydroxy*-x-*chloroacetylnaphthalene*.—The low-melting product of the Friedel–Crafts reaction (3 g.), hydrochloric acid (30 c.c.; 20%), and acetic acid (30 c.c.) were heated for ¾ hour at 95°, and the solution diazotised as above. After 35 days at room temperature the black precipitate was collected (2·03 g.) and extracted with alcohol (500 c.c.), and the extract concentrated, giving pale brown needles (0·21 g.). Recrystallisation from benzene gave yellow needles of 2-*hydroxy*-x-*chloroacetylnaphthalene*, m. p. 143—144° (Found: C, 65·9; H, 4·3; Cl, 15·4. $C_{12}H_9O_2Cl$ requires C, 65·3; H, 4·1; Cl, 16·1%).

2-*Amino*-3-*naphthyldimethylcarbinol*.—Methyl 3-amino-2-naphthoate (2 g.) in ether (200 c.c.) was added to methylmagnesium iodide (from 1·44 g. of magnesium) in ether (25 c.c.) during 1 hour at 0° with stirring, an orange complex being formed. The mixture was boiled under reflux for 4 hours, decomposed with ammonium chloride and ice, and the ethereal layer separated. Removal of the solvent gave an orange solid (1·58 g.), which on crystallisation from ether–ligroin (b. p. 60—80°) formed orange needles of 2-*amino*-3-*naphthyldimethylcarbinol*, m. p. 104—105° (Found: C, 77·0; H, 7·3. $C_{13}H_{15}ON$ requires C, 77·6; H, 7·5%).

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