Some Heterocyclic Structures derived from Acenaphthene.

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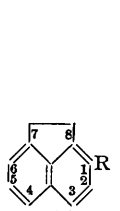
The conversion of 1-, 2-, and 3-aminoacenaphthene into some acenaphtheno-pyridine, -quinoline, and -*iso*quinoline derivatives is reported.

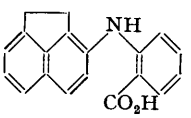
Conversion of 1-, 2-, and 3-aminoacenaphthene into some heterocyclic structures, required for biological study, is reported.

Morgan and Harrison (*J. Soc. Chem. Ind.*, 1930, **49**, 413T) obtained 1-nitroacenaphthene (I; R = NO_2) by nitration of the hydrocarbon with acetyl or benzoyl nitrate in acetic anhydride. This method is unsuitable for large-scale work and indeed, in our hands, gave none of the required product, the 3-nitro-isomer alone being isolated. We consequently studied other routes to (I; R = NH_2), ultimately preparing it from 1-acetylacenaphthene.

Condensation of acenaphthene with acetic acid–hydrogen fluoride gave 1-acetylacenaphthene (I; R = Ac) (Fieser and Hershberg, *J. Amer. Chem. Soc.*, 1939, **61**, 1272), smoothly oxidised by sodium hypochlorite to 1-acenaphthoic acid (I; R = CO_2H) (cf. Fieser and Hershberg, *loc. cit.*). Esterification of the last compound with diazomethane furnished the methyl ester, which was converted into the hydrazide. Successive action of nitrous acid and dilute hydrochloric acid, however, failed to give (I; R = NH_2), *s*-di-1-acenaphthenylurea being the sole product. Formation of (I; R = NH_2) in low yield was achieved by the reaction sequence: (I; R = CO_2H) ⟶ acid chloride ⟶ azide ⟶ 1-aminoacenaphthene (*ca.* 30%) (admixed with larger quantities of *s*-di-1-acenaphthenylurea). Somewhat better results followed Beckmann rearrangement of 1-acenaphthenyl methyl ketoxime with phosphorus pentachloride, 1-acetamidoacenaphthene being obtained in 40% yield. The preparative method finally adopted was based upon Smith's extension of the Schmidt reaction (Smith, *ibid.*, 1948, **70**, 320) in which (I; R = Ac) was treated with sodium azide in molten trichloroacetic acid to give 1-acetamidoacenaphthene (I; R = NHAc) in excellent yield. Hydrolysis was best accomplished with alcoholic hydrochloric acid. Concentrated sulphuric acid could not be employed in this instance, as immediate sulphonation occurred even at 0° [cf. our earlier attempts (*J.*, 1948, 1713) to effect the Schmidt reaction on (I; R = Ac) in concentrated sulphuric acid].



(I)



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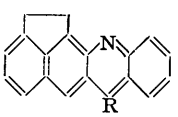
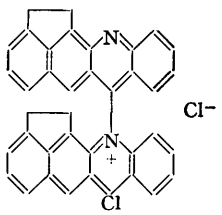


(III)



(IV)

Attempts to convert 1-aminoacenaphthene (I; R = NH_2) into pyrido(2′ : 3′-1 : 2)-acenaphthene proved wholly unsuccessful. Thus the normal conditions of the Skraup reaction led to extensive decomposition with recovery of a trace of unused base. No better results derived from (i) the addition of ferrous sulphate and/or boric acid (cf. Cohn, *J. Amer. Chem. Soc.*, 1930, **52**, 3685), (ii) the replacement of nitrobenzene as oxidant by arsenic oxide, or (iii) the substitution of 1-acetamidoacenaphthene for the base under the "mild" conditions recommended by Manske and his co-workers (*Canad. J. Res.*, 1941, **19**, *B*, 318). Condensation with paraldehyde or with acetaldehyde–pyruvic acid were likewise unsuccessful.

1-Aminoacenaphthene and *o*-chlorobenzoic acid condensed readily in amyl-alcoholic solution in the presence of copper bronze to give *N*-1′-acenaphthenylanthranilic acid (II). Ring closure of this compound to the corresponding acridine analogue could not be

achieved by concentrated sulphuric acid at 100° which caused rapid sulphonation (cf. above) or by phosphoric oxide in syrupy phosphoric acid at 150°, which was without effect. Reaction with phosphorus oxychloride led to a dark red crystalline compound which, though giving analyses correct for the expected 4′-chloroacenaphtheno(1′ : 2′-2 : 3)-quinoline (III; R = Cl), is probably best formulated as 1-[acenaphtheno(1′ : 2′-2 : 3)-4-quinolyl]-4-chloroacenaphtheno(1′ : 2′-2 : 3)quinolinium chloride (IV). Thus the red colour, relatively high melting point, and low alcoholic solubility accord well with the structure (IV). Again, reduction with sodium amalgam, zinc dust and acetic acid, or aluminium foil in ethanol led only to unidentified amorphous products of high melting point. Finally, the electrical conductivity of the compound in nitrobenzene at room temperature was approximately 20 times that of an equimolar solution of phenol, an observation which argues a high degree of ionisation. Distillation of the red quaternary salt (IV) with zinc dust under reduced pressure led to the formation of acenaphtheno-(1′ : 2′-2 : 3)quinoline (III; R = H) in low yield. The bright red colour of this base accords with the established effect of the heterocyclic nitrogen atom on the colour of linear polycyclic systems.

Attempts to extend Hollingsworth and Petrow's tetrahydrophenanthridine synthesis (*J.*, 1948, 1537) to 1-aminoacenaphthene were not successful.

Preparation of 2-aminoacenaphthene proved troublesome. Morgan and Harrison (*J. Soc. Chem. Ind.*, 1930, **49**, 413T) prepared this compound by the following reaction sequence: 3-formamidoacenaphthene ⟶ 3-amino-2-nitroacenaphthene ⟶ 3-iodo-2-nitroacenaphthene ⟶ 2-aminoacenaphthene, but the overall yields were low.

In our hands, nitration of 3-formamidoacenaphthene seldom gave yields approaching the 75% claimed by Morgan and Stanley (*ibid.*, 1925, **44**, 493T). In an attempt to improve this stage, 3-toluene-*p*-sulphonamidoacenaphthene was prepared and nitrated but the yield of 2-nitro-amine was no better. The conversion of this nitro-amine into 3-iodo-2-nitroacenaphthene proved highly unsatisfactory, even under the modified diazotisation conditions of Hodgson and Walker (*J.*, 1933, 1620) and had perforce to be abandoned. The improved porcedure ultimately adopted was to reduce the diazonium salt from 3-amino-2-nitroacenaphthene with cuprous oxide in methanol at 60° (Hodgson and Turner, *ibid.*, 1942, 748) to 2-nitroacenaphthene, which was conveniently hydrogenated to 2-amino-acenaphthene with hydrogen–platinum in excellent overall yield.

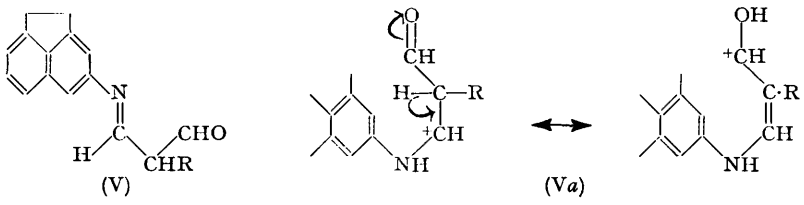
2-Aminoacenaphthene failed to undergo the Skraup reaction as modified by Cohn (*loc. cit.*). Its conversion into the pyrido(2′ : 3′-2 : 3)acenaphthene system (VI), which bears a formal resemblance to 1 : 2-dihydroergotine, was ultimately achieved in disappointing overall yields by adapting the method of Uhle and Jacobs (*J. Org. Chem.*, 1945, **10**, 76) for converting 3-aminonaphthastyril into (±)-dihydrolysergic acid.

Reaction of 2-aminoacenaphthene with cyanomalondialdehyde furnished 2-cyano-3-2′-acenaphthenyliminopropanal (V; R = CN) in *ca.* 20% yield. Similar reaction with nitromalondialdehyde gave the 2-nitro-derivative (V; R = NO_2), but in only 5% yield.

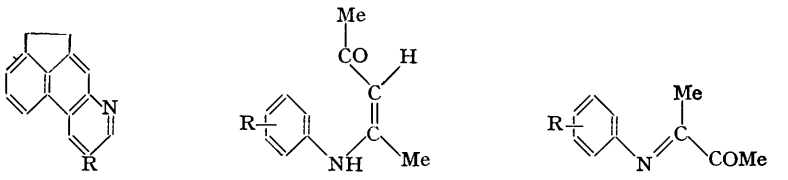
Ring closure of (V; R = CN) by fusion with zinc chloride, followed by hydrolysis (cf. Uhle and Jacobs, *loc. cit.*), furnished a 20% yield of a gelatinous amorphous product which failed to crystallise. Its constitution as (VI; R = CO_2H) was nevertheless established by esterification with methanolic hydrochloric acid, the methyl ester (VI; R = CO_2Me) being crystalline. The low yield of product obtained in the cyclisation undoubtedly arose from the *trans*-configuration of the anil (V; R = CN) [see de Gaouck and Le Fèvre (*J.*, 1938, 741; 1939, 1392; Petrow, *loc. cit.*)] which must undergo thermal isomerisation to a *cis*-structure before ring closure. In accordance with this view we find that conversion of (V) into (VI) is facilitated by removing the steric factors inhibiting ring closure by (*a*) adding a proton to the azomethine link: $-\overset{\curvearrowleft}{N}{=}CH- \xrightarrow{H^+} -NH-\overset{+}{C}N-$ and (*b*) reducing the azomethine bond.

This concept of proton addition to the azomethine *N*-atom finds support in the work of Roberts and Taylor (*ibid.*, 1927, 1832; cf. Coombes, *Bull. Soc. chim.*, 1888, **49**, 90; *Compt. rend.*, 1887, **106**, 124) who studied the conversion of certain substituted anils of acetylacetone into the quinolines by brief heating with concentrated sulphuric acid. Their results led

them to assign the *cis*-anilino-structure (VII) to anils undergoing ring closure under these conditions, reserving the anil structure (VIII) for those compounds in which only hydrolysis to the components took place. This explanation, however, can no longer be regarded as adequate. We now find that the infra-red absorption spectra of *o*-, *m*-, and *p*-chloro-anils of acetylacetone (of which only the *m*-isomer yields the quinoline base with concentrated sulphuric acid) have similar absorption bands at 6·2 μ characteristic of the azomethine link but fail to show bands at 6·5, 7·6, and 7·8 μ characteristic of the (chloro)-anilino-group. All three compounds must consequently be assigned structures of type (VIII). Their differing behaviour to concentrated sulphuric acid is thus unlikely to reside in structural differences represented by (VII) and (VIII) but it is readily explained by differences in electron-availability at the N atom. Conversion of (V) into (VI) *via* the resonating cation (V*a*) may consequently be regarded as a special case of the general reaction mechanism for quinoline formation previously proposed by Morley and Simpson (*J.*, 1948, 2024).



(V) (V*a*)



(VI) (VII) (VIII)

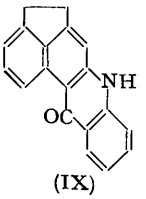
In accordance with (*a*) above we find that brief reaction of (V; R = CN) with hot concentrated sulphuric acid leads to the amide (VI; R = $CO{\cdot}NH_2$) in *ca.* 50% yield. By extending the time of heating, the corresponding acid (VI; R = CO_2H) is obtained in similar yield and may be characterised by conversion into the methyl and the ethyl ester. Syrupy phosphoric acid–phosphoric oxide at 100° may also be employed to convert the nitrile into the amide but the yield in this case is only 30%. The nitro-compound (V; R = NO_2), in contrast, fails to cyclise under these experimental conditions, probably owing to the lower electron-availability at the methine-N atom due to the $+I$ effect of the proximate nitro-group.

An alternative route to (VI) lies in the application of (*b*) (above) in which the nitrile (V; R = CN) and the nitro-compound (V; R = NO_2) are heated with anhydrous formic acid (cf. Hollingsworth and Petrow, *loc. cit.*). Reduction of the methine link accompanied by cyclisation then readily gives the required pyridines in 40% and 20% yield, respectively.

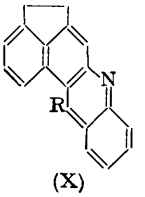
2-Aminoacenaphthene did not condense with *o*-chlorobenzoic acid and copper bronze in amyl alcohol. Results were better in *cyclo*hexanol, a high-melting acidic, presumably impure *N*-2′-acenaphthenylanthranilic acid being obtained in *ca.* 25% yield. In attempts to purify this material through esterification with methanolic hydrochloric acid, a surprisingly ready ring closure gave 1 : 4-dihydro-4-oxo-acenaphtheno(2′ : 3′-2 : 3)quinoline (IX). This afforded the parent (X; R = H) by direct reduction with amalgamated aluminium foil (Albert and Ritchie, *J. Soc. Chem. Ind.*, 1941, **60**, 120) or reaction with phosphorus oxychloride to give 4′-chloro-compound (X; R = Cl), followed by reduction with sodium amalgam.

Reaction of 2-aminoacenaphthene with 2-formyl*cyclo*hexanone gave the Schiff's base, which passed smoothly into the tetrahydro*iso*quinoline (XI) in hot anhydrous formic acid (Hollingsworth and Petrow, *loc. cit.*).

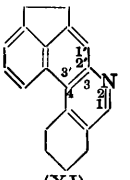
3-Aminoacenaphthene and 2-formyl*cyclo*hexanone gave a Schiff's base, readily converted into the tetrahydroquinoline (XII) by Petrow's method (*loc. cit.*). Its dehydrogenation to the fully aromatic system (XIII; R = H) could not be effected by such reagents as selenium at 260°, sulphur in boiling benzyl benzoate (Simpson, *J.*, 1939, 755), or chloranil in xylene (Barclay and Campbell, *J.*, 1945, 530), or by distillation with lead dioxide (Braun and Gruber, *Ber.*, 1922, **55**, 1710). The base (XIII; R = H) was



(IX)



(X)



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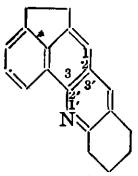
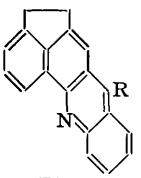
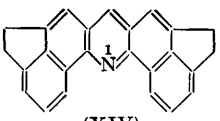


(XII)



(XIII)



(XIV)

consequently prepared from *N*-3′-acenaphthenylanthranilic acid by reaction with phosphorus oxychloride, giving (XIII; R = Cl), followed by reduction with sodium amalgam.

Condensation of 3-aminoacenaphthene with methylene iodide gave a pale yellow base, $C_{25}H_{17}N$, which has been assigned structure (XIV).

Experimental

1-*Acenaphthoic Acid*.—A solution of sodium hypochlorite, prepared by passing chlorine at 0° into water (10 ml.) containing sodium hydroxide (3·7 g.) until neutral to litmus, was treated with further sodium hydroxide (0·7 g.) and the mixture added gradually (20 min.) with shaking to a solution of 3-acetylacenaphthene (15 g.) (Fieser and Hershberg, *loc. cit.*) in methanol (40 ml.) at 60°. The mixture was finally heated at 70° for 30 min. and the methanol removed by evaporation. On acidification, 1-acenaphthoic acid was precipitated as an almost pure, white crystalline powder (1·5 g.), m. p. 243°.

The finely powdered acid (1·98 g.) was added gradually to diazomethane (0·8 g.) in dry ether (25 ml.). After 1½ hr. the ether was removed and the product crystallised twice from aqueous ethanol. *Methyl* 1-*acenaphthoate* (1·75 g.) formed pale yellow needles, m. p. 81° (Found: C, 79·5; H, 6·0. $C_{14}H_{12}O_2$ requires C, 79·5; H, 5·7%).

This ester (1·0 g.) and 90% hydrazine hydrate (3·0 ml.) were refluxed together for 6½ hr. On cooling, 1-*acenaphthoylhydrazine* (0·8 g.) separated as colourless plates, m. p. 178° (from ethanol) (Found: C, 73·3; H, 5·9. $C_{13}H_{12}ON_2$ requires C, 73·5; H, 5·7%).

s-*Di*-1-*acenaphthenylurea*.—The hydrazide (0·5 g.), dissolved in warm dioxan (7 ml.), was added, with vigorous shaking, to 2N-hydrochloric acid (13 ml.) and ice (12 g.). To the resulting fine suspension, a solution of sodium nitrite (0·2 g.) in a little water was added dropwise during 30 min. The resulting solid was collected and heated to 100° with 2N-hydrochloric acid (25 ml.) for 10 min. The mixture was filtered, and the residue washed with water. No basic material could be isolated from the washings, but after two crystallisations from nitrobenzene the residue gave s-*di*-1-*acenaphthenylurea*, m. p. 280° (Found: C, 82·4; H, 5·5; N, 7·4. $C_{25}H_{20}ON_2$ requires C, 82·4; H, 5·5; N, 7·7%).

1-*Acenaphthazide*.—1-Acenaphthoyl chloride (1·0 g., prepared by Fieser and Hershberg's method, *loc. cit.*) in dry acetone (25 ml.) was treated at 10° during 5 min. with a solution of sodium azide (1·3 g.) in water (6 ml.). After 30 min., dilution with ice-water (35 ml.) precipitated a pale solid (0·85 g.). After crystallisation from aqueous acetone 1-*acenaphthazide* (0·7 g.) formed yellow needles, m. p. 104° (Found: C, 70·1; H, 4·0; N, 18·6. $C_{13}H_9ON_3$ requires C, 70·0; H, 4·1; N, 18·8%).

The azide (0·65 g.) in benzene (6·5 ml.) was refluxed for 3 hr. Concentrated hydrochloric acid (5 ml.) was then added and heating continued for a further 1½ hr. Water (100 ml.) was added, the benzene layer removed, and the aqueous layer extracted with two 25-ml. portions of ether, which were combined with the benzene. Basifying the aqueous layer alkaline with potassium hydroxide precipitated a light brown solid (0·15 g.) which was identified as 1-amino-acenaphthene by benzoylation to 1-benzamidoacenaphthene, pale yellow needles, m. p. and mixed m. p. 207°. The benzene–ether solution was washed with water, dried and evaporated. The residue crystallised from nitrobenzene as light brown plates of *s*-di-1-acenaphthenylurea, m. p. 280°, not depressed on admixture with a specimen obtained as above.

1-*Acetylacenaphthene oxime*, prepared from 1-acetylacenaphthene (5 g.) in ethanol (30 ml.) and hydroxylamine hydrochloride (2·5 g.), sodium acetate (5·0 g.), and water (10 ml.) under reflux for 2 hr., separated (5·0 g.) in white needles, m. p. 149—150° (Found : C, 79·5; H, 6·3; N, 6·6. $C_{14}H_{13}ON$ requires C, 79·5; H, 6·2; N, 6·5%).

Beckmann Rearrangement of the Oxime.—The foregoing compound (1·0 g.) in dry ether (35 ml.) was treated gradually, with shaking, with phosphorus pentachloride (1·5 g.), a yellow gum separating. The ether was evaporated and the residue decomposed with ice-water. The semi-solid product, on crystallisation from aqueous ethanol (charcoal), gave felted needles (0·4 g.) of 1-acetamidoacenaphthene, m. p. 191—192° (Found : C, 79·3; H, 6·1; N, 6·6. Calc. for $C_{14}H_{13}ON$: C, 79·5; H, 6·2; N, 6·6%).

1-*Acetamidoacenaphthene.*—1-Acetylacenaphthene (20 g.) in molten trichloroacetic acid (100 g.) at 60° was treated gradually with stirring with finely powdered sodium azide (10 g.). The reaction was completed by heating the mixture at 65° for 1 hr. with occasional stirring. Water (150 ml.) was added in small portions with thorough mixing and the resultant magma filtered at the pump and washed with a little 50% ethanol. The product (18 g.) formed yellowish needles and was sufficiently pure for hydrolysis to the amine. A portion crystallised from 50% ethanol as white felted needles, m. p. 192° (Morgan and Harrison, *loc. cit.*, give m. p. 192—193°).

1-*Aminoacenaphthene.*—The foregoing compound (18 g.) in ethanol (500 ml.) and concentrated hydrochloric acid (25 ml.) was refluxed for 12 hr., after which the ethanol was removed by distillation. The residue was boiled with water (500 ml.), concentrated hydrochloric acid (50 ml.), and charcoal, and filtered while hot. When cooled and made ammoniacal, the filtrate deposited 1-aminoacenaphthene (11·0 g.; m. p. 75°). Crystallisation from light petroleum gave nearly white needles, m. p. and mixed m. p. 82° (lit., m. p. 81·5°).

N-1′-*Acenaphthenylanthranilic Acid* (II).—*o*-Chlorobenzoic acid (3·15 g.) in amyl alcohol (15 ml.) was boiled with anhydrous potassium carbonate (2·75 g.) for 1 min. (to expel water and carbon dioxide). 1-Aminoacenaphthene (3·4 g.) and copper bronze (0·2 g.) were added and the mixture heated under reflux in an oil-bath for 4 hr. The amyl alcohol was removed in steam, and the residue dissolved in boiling water (250 ml.; charcoal) and filtered hot. Acidification gave N-1′-*acenaphthenylanthranilic acid* (2·65 g.), m. p. 241° (Found : C, 78·7; H, 5·1; N, 4·8. $C_{19}H_{15}O_2N$ requires C, 78·9; H, 5·2; N, 4·9%), needles from ethanol.

Cyclisation of N-1′-*Acenaphthenylanthranilic Acid.*—The acid (3·0 g.) and phosphorus oxychloride (25 ml.) were refluxed for 1 hr. Chloroform (250 ml.) was added and the solution poured in a thin stream into a well-stirred mixture of concentrated aqueous ammonia and crushed ice. The lower layer was separated, washed with water, and dried ($CaCl_2$), and the solvent was removed. The residue (1·0 g.) crystallised from ethanol to give 1-[*acenaphtheno*-(1′ : 2′-2 : 3)-4-*quinolyl*]-4-*chloroacenaphtheno*(1′ : 2′-2 : 3)*quinolinium chloride* (IV), dark red needles, m. p. 192° (Found : C, 78·5; H, 4·4; Cl, 12·1. $C_{19}H_{12}NCl$ requires C, 78·7; H, 4·2; Cl, 12·3%).

Acenaphtheno(1′ : 2′-2 : 3)*quinoline* (III; R = H).—The foregoing compound (1·0 g.) was finely ground with zinc dust (2·0 g.), and the powder distilled at 15 mm. A dark red oil distilled and was extracted with benzene (15 ml.). The combined benzene extracts from two such distillations were filtered and chromatographed on alumina (40 g.) (Brockman, Grade 1 alumina used throughout). Elution with benzene containing 1% of methanol gave two bands. The first, a narrow yellow band, was rejected. The second, eluted with 50 ml. of the above solvent, formed a broad red band and on evaporation gave an orange-red solid which crystallised from benzene or ethanol, forming red prisms (8 mg.) of *acenaphtheno*(1′ : 2′-2 : 3)*quinoline*, m. p. 153° (Found : C, 89·2; H, 5·2; N, 5·6. $C_{19}H_{13}N$ requires C, 89·4; H, 5·1; N, 5·5%).

3-*Toluene*-p-*sulphonamidoacenaphthene.*—3-Aminoacenaphthene (4·7 g.) in dry pyridine (50 ml.) was cooled in ice and toluene-*p*-sulphonyl chloride (5·4 g.) added with stirring during 5 min. The mixture was set aside for 16 hr. and then poured on ice and concentrated hydro-

chloric acid (50 ml.). The precipitate was collected and crystallised from ethanol giving the *toluenesulphonamide* in grey needles (Found: N, 4·4. $C_{19}H_{17}O_2NS$ requires N, 4·3%).

2-*Nitro*-3-*toluene*-p-*sulphonamidoacenaphthene*.—Finely ground 3-toluene-*p*-sulphonamidoacenaphthene (4·6 g.) in acetic acid (30 ml.) at 0—10° was treated gradually with concentrated nitric acid (14 ml.). After 1 hr. the yellow precipitate was collected and crystallised from ethanol. 2-*Nitro*-3-*toluene*-p-*sulphonamidoacenaphthene* (1·8 g.) formed yellow needles, m. p. 180° (Found: C, 61·8; H, 4·1. $C_{19}H_{16}O_4N_2S$ requires C, 61·9; H, 4·3%).

2-*Nitroacenaphthene*.—3-Amino-2-nitroacenaphthene (9·0 g.) in glacial acetic acid (90 ml.) and concentrated sulphuric acid (45 ml.) was treated slowly at room temperature with finely powdered sodium nitrite (9·0 g.). The mixture was set aside for 1 hr. and then added during 30 min. to a vigorously stirred suspension of freshly prepared cuprous oxide (18 g.) in methanol (350 ml.) at 60°. Nitrogen was evolved and an orange solution formed. Water (1 l.) was added and the resultant precipitate filtered off and washed with sodium carbonate solution and then with water. Extraction of the crude product with ethanol, followed by concentration of the extract, furnished 2-*nitroacenaphthene* (5·3 g.) as golden-yellow needles, m. p. 129° (Found: C, 72·3; H, 4·4; N, 7·0. $C_{12}H_9O_2N$ requires C, 72·4; H, 4·5; N, 7·0%) after one recrystallisation.

2-*Aminoacenaphthene*.—2-Nitroacenaphthene (10·0 g.), ethyl acetate (200 ml.), and platinum oxide (1 g.) were shaken in hydrogen at 20°/2 atm. until absorption was complete. The catalyst was removed and the solvent evaporated. The dark residue was dissolved in benzene (25 ml.) and percolated through alumina (10 g.), the column being washed with a further 10 ml. of benzene. The combined eluates were evaporated to 15 ml. and light petroleum (10 ml.; b. p. 60—80°) added, 2-aminoacenaphthene (7·5 g.) crystallising rapidly as buff-coloured needles, m. p. 87°.

3-2′-*Acenaphthenylimino*-2-*cyanopropanal* (V; R = CN).—Cyanoacetaldehyde diethyl acetal (10·0 g.), ethyl formate (6 g.), and sodium powder (3·0 g.) in dry ether (25 ml.) were left for 16 hr. at room temperature. Ice-water (20 ml.) was added and the aqueous layer, containing the sodium derivative of cyanomalondialdehyde, run dropwise into a well-stirred suspension of finely ground 2-aminoacenaphthene (5 g.) in 2% hydrochloric acid (300 ml.). The dark brown precipitate was collected and triturated with 50% acetone–methanol, and the yellow residue collected and crystallised from ethanol. 3-2′-*Acenaphthenylimino*-2-*cyanopropanal* (2·0 g.) formed yellow needles, m. p. 209° (Found: C, 77·5; H, 5·0. $C_{16}H_{12}ON_2$ requires C, 77·5; H, 4·9%).

Pyrido(2′ : 3′-2 : 3)*acenaphthene*-5′-*carboxyamide* (VI; R = $CO{\cdot}NH_2$).—To the foregoing compound (0·3 g.), dissolved in syrupy phosphoric acid (1·0 ml.), phosphoric oxide (2·5 g.) was added with stirring, the temperature rising to 100°. After 1 hr., ice (50 g.) was added together with an excess of aqueous ammonia. The precipitate was collected and crystallised twice from ethanol. The crude amide (0·1 g.) formed yellow needles, m. p. 257°. A small quantity of the carboxylic acid (see below) was isolated from the ammoniacal filtrate by neutralisation.

The *methosulphate*, orange needles (Found: N, 7·6. $C_{18}H_{18}O_5N_2S$ requires N, 7·5%), was prepared by treating the amide (50 mg.) in nitrobenzene (1·0 ml.) with methyl sulphate (0·05 ml.), adding benzene (5 ml.), and washing the precipitate with benzene.

Pyrido(2′ : 3′-2 : 3)*acenaphthene*-3-*carboxylic Acid* (VI; R = CO_2H).—(*a*) The nitrile (V; R = CN) (3·0 g.) and anhydrous, finely ground zinc chloride (1·5 g.) were heated slowly to 250° in an air-bath and this temperature maintained for 10 min. The glass obtained on cooling was ground, extracted 3 times with water, and boiled for 1 hr. with 18% hydrochloric acid (150 ml.), and the mixture filtered. The filtrate was evaporated to dryness *in vacuo* and the residue extracted with an excess of dilute ammonia solution. Neutralisation to litmus gave the acid (VI; R = CO_2H) as a pale yellow gelatinous solid (0·16 g.).

(*b*) The nitrile (0·5 g.) was added gradually with stirring to concentrated sulphuric acid (10 ml.), and the mixture warmed to 100° for 1 hr. Ice (30 g.) was added and the solution made ammoniacal and filtered. Neutralisation of the filtrate gave the acid (0·25 g.).

The crude acid (0·2 g.) was boiled with 3% methanolic hydrochloric acid (5·0 ml.) for 3 hr. On dilution, the *methyl ester* was precipitated. It separated from aqueous methanol in pale yellow needles, m. p. 170° (Found: C, 77·5; H, 4·8; N, 5·1. $C_{17}H_{13}O_2N$ requires C, 77·5; H, 4·9; N, 5·3%). The *ethyl ester*, similarly prepared, formed long yellow needles, m. p. 126° (Found: C, 78·1; H, 5·2. $C_{18}H_{15}O_2N$ requires C, 78·0; H, 5·4%), after crystallisation from ethanol.

3-2-*Acenaphthenylimino*-2-*nitropropanal* (V; R = NO_2).—Mucobromic acid (5 g.) was added in small portions with stirring to a suspension of finely powdered sodium nitrite (5 g.) in water (5 ml.) and ethanol (7 ml.). The mixture was warmed slowly to 50° until effervescence ceased

and then rapidly cooled to −20°. The sodium derivative of nitromalondialdehyde was collected, washed rapidly with ice-cold 50% aqueous ethanol, and dissolved in water (20 ml.). This solution was added dropwise with stirring to a suspension of finely ground 2-aminoacenaphthene (3·0 g.) in 1·5% hydrochloric acid (200 ml.). The resulting dark brown precipitate was crystallised once from ethanol and twice from 60% acetic acid. The *product* (0·4 g.) formed yellow needles, m. p. 210° (Found: C, 67·0; H, 4·3; N, 10·3. $C_{15}H_{12}O_3N_2$ requires C, 67·2; H, 4·5; N, 10·4%).

5′-*Cyanopyrido*(2′ : 3′-2 : 3)*acenaphthene* (VI; R = CN).—The nitrile (V; R = CN) (0·1 g.) and anhydrous formic acid (2·0 ml.) were heated under reflux for 10 hr., then the mixture was poured on ice and aqueous ammonia. The precipitate was collected and crystallised from dilute ethanol. The *product* (15 mg.) formed brownish squat needles, m. p. 201° (Found: C, 83·4; H, 4·5. $C_{16}H_{10}N_2$ requires C, 83·5; H, 4·5%).

5′-*Nitropyrido*(2′ : 3′-2 : 3)*acenaphthene* (VI; R = NO_2), prepared by heating the nitrile (V; R = NO_2) (0·75 g.) with anhydrous formic acid (6·0 ml.) under reflux for 17 hr., formed orange-yellow needles, m. p. 191° (Found: C, 71·6; H, 3·9; N, 11·4. $C_{15}H_{10}O_2N_2$ requires C, 72·0; H, 4·0; N, 11·2%), after crystallisation from ethyl acetate.

1 : 4-*Dihydro*-4-*oxoacenaphtheno*(2′ : 3′-2 : 3)*quinoline* (IX).—2-Aminoacenaphthene (1·7 g.), *o*-chlorobenzoic acid (1·6 g.), anhydrous potassium carbonate (1·5 g.), *cyclo*hexanol (10 ml.), and copper bronze (0·1 g.) were heated under reflux in an oil-bath for 3 hr. The *cyclo*hexanol was removed in steam, and the dark residue extracted with boiling 2N-sodium carbonate (150 ml.) and filtered hot. On acidification, crude *N*-2′-acenaphthenylanthranilic acid (0·75 g.) was obtained, which could not be recrystallised.

This product was dissolved in 10 ml. of ethanol saturated with hydrogen chloride and the solution heated under reflux for 1 hr. The yellow crystalline solid which separated on cooling was collected, boiled with dilute ethanolic sodium hydroxide to remove acidic material and esters, and crystallised from ethanol. The *quinoline* (0·25 g.) formed cream-coloured plates which sublimed, without melting, at 310° (Found: C, 83·9; H, 4·7. $C_{19}H_{13}ON$ requires C, 84·1; H, 4·7%).

4-*Chloroacenaphtheno*(2′ : 3′-2 : 3)*quinoline* (X; R = Cl).—The foregoing compound (0·2 g.) and phosphorus oxychloride (1·0 ml.) were heated under reflux for 1 hr., giving the *chloro*-derivative (0·15 g.) as orange-yellow needles, m. p. 171° (Found: C, 4·8; Cl, 12·2. $C_{19}H_{12}NCl$ requires N, 4·9; Cl, 12·3%).

Acenaphtheno(2′ : 3′-2 : 3)*quinoline* (X; R = H).—(*a*) The foregoing compound (0·2 g.), 4% sodium amalgam (10 g.), ethanol (20 ml.), and water (10 ml.) were heated under reflux for 2 hr. The mercury was separated, the alcohol removed *in vacuo*, and the residue extracted with benzene (5 ml.). The benzene extract was percolated through a short column of alumina (5 g.), which was washed with a further 10 ml. of benzene. The combined eluates were evaporated to dryness under reduced pressure and the residue crystallised from dilute ethanol. *Acenaphtheno*(2′ : 3′-2 : 3)*quinoline* (0·09 g.) formed yellow needles, m. p. 188° (Found: N, 5·5. $C_{19}H_{13}N$ requires N, 5·5%).

(*b*) 1 : 4-Dihydro-4-oxoacenaphtheno(2′ : 3′-2 : 3)quinoline (50 mg.) in ethanol (5 ml.) containing amalgamated aluminium foil (0·5 g.) was refluxed for 2 hr. The mixture was filtered and the filtrate evaporated to dryness *in vacuo*. The residue was extracted with benzene (10 ml.), the extract evaporated to dryness, and the residue crystallised from dilute ethanol. The base (15 mg.) formed yellow needles, m. p. 188°, not depressed on admixture with a sample prepared as under (*a*).

2-(2-*Oxo*cyclo*hexylmethyleneamino*)*acenaphthene*.—Prepared from 2-aminoacenaphthene by Hollingsworth and Petrow's method (*loc. cit.*) this *compound* formed pale yellow needles, m. p. 229° (Found: N, 4·7. $C_{19}H_{19}ON$ requires N, 5·0%), after purification from ethanol.

5 : 6 : 7 : 8-*Tetrahydroacenaphtheno*(2′ : 3′-3 : 4)iso*quinoline* (XI).—The foregoing derivative (1·75 g.) and anhydrous formic acid (15 ml.) were heated under reflux for 24 hr., then the bulk of the formic acid was removed by distillation *in vacuo*. The residue was poured on ice (10 g.) and concentrated aqueous ammonia (5 ml.), and the solids were collected. The product was dissolved in ethanol (10 ml.), and a solution of picric acid (2 g.) in hot ethanol (5 ml.) added. After 16 hr. the precipitated picrate was collected and the base regenerated by shaking it in benzene (20 ml.) with 10% lithium hydroxide solution. The benzene layer was washed with water and evaporated to dryness. The residual iso*quinoline* crystallised from aqueous ethanol in light orange needles, m. p. 162° (Found: C, 88·1; H, 6·7; N, 5·5. $C_{19}H_{17}N$ requires C, 88·0; H, 6·6; N, 5·4%).

5 : 6 : 7 : 8-*Tetrahydroacenaphtheno*(2′ : 3′-2 : 3)*quinoline* (XII).—3-(2′-Oxo*cyclo*hexyl-

methyleneamino)acenaphthene (5·5 g.; Hollingsworth and Petrow, *loc. cit.*), 3-aminoacenaphthene hydrochloride (3·4 g.), fused zinc chloride (2·6 g.), and absolute ethanol (100 ml.) were refluxed for 28 hr. During the first 9 hr. red crystals slowly separated, which later dissolved. The mixture was cooled and filtered. The residue was warmed for 10 min. with an excess of 2N-sodium hydroxide, cooled, and filtered. After two crystallisations from ethanol, the residue gave the *quinoline* (2·7 g.) as orange needles, m. p. 136° (Found: C, 88·2; H, 6·7; N, 5·6. $C_{19}H_{17}N$ requires C, 88·0; H, 6·6; N, 5·4%). The product fluoresced an intense blue in ultra-violet light.

4-*Chloroacenaphtheno*(2′ : 3′-2 : 3)*quinoline* (XIII; R = Cl).—N-3′-*Acenaphthenylanthranilic acid* formed (36%) golden-yellow plates, m. p. 234° (Found: C, 79·0; H, 5·2; N, 4·9. $C_{19}H_{15}O_2N$ requires C, 78·9; H, 5·2; N, 4·9%). It (7·65 g.) and phosphorus oxychloride (50 ml.) were refluxed for 1 hr. The mixture was cooled, chloroform (250 ml.) added, and the solution poured in a thin stream into a well-stirred mixture of ice and aqueous ammonia (*d* 0·88). The chloroform layer was separated, washed with water, dried ($CaCl_2$), and evaporated to dryness. The orange residue was crystallised twice from ethanol containing a trace of ammonia. The *product* (5·5 g.) formed pale yellow needles, m. p. 183° (Found: C, 78·8; H, 4·4; N, 4·9. $C_{19}H_{12}NCl$ requires C, 78·8; H, 4·2; N, 4·9%).

Acenaphtheno(3′ : 2′-2 : 3)*quinoline* (XIII; R = H).—The foregoing compound (4·1 g.) in 90% aqueous ethanol (380 ml.) containing 4% sodium amalgam (125 g.) was refluxed for 16 hr., then the mercury was removed and the ethanolic solution concentrated to 200 ml. On cooling, the *base* separated. After two crystallisations from ethanol it formed silky yellow needles (2·15 g.), m. p. 166° (Found: C, 89·2; H, 5·4; N, 5·8. $C_{19}H_{13}N$ requires C, 89·4; H, 5·1; N, 5·8%). The *picrate* formed small needles, m. p. 268° (Found: N, 11·2. $C_{19}H_{13}N,C_6H_3O_7N_3$ requires N, 11·5%), after crystallisation from ethanol.

Diacenaphtheno(3′ : 2′-2 : 3)(2″ : 3″-5 : 6)*pyridine* (XIV).—To 3-aminoacenaphthene (10·2 g.) at 130°, methylene iodide (8·9 g.) was added. The temperature was raised slowly to 135°, whereupon a vigorous reaction took place. The temperature of the bath was finally raised to 170° for 15 min. The cooled residue was extracted with boiling ethanol (350 ml.) containing potassium hydroxide (1·0 g.), and the extracts were diluted with water (400 ml.). The brown precipitate (8·0 g.) was collected and crystallised three times from boiling pyridine. The *product* (2·4 g.) formed small pale yellow prisms, m. p. 298° (decomp.) (Found: C, 91·0; H, 5·0; N, 4·5. $C_{25}H_{17}N$ requires C, 90·6; H, 5·1; N, 4·3%) (cf. Morgan and Harrison, *J. Soc. Chem. Ind.*, 1930, **49**, 419T).

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