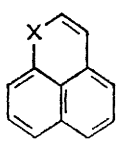
541. *The Synthesis of Heterocyclic Analogues of Phenalene (Perinaphthene), containing one Hetero-atom.*

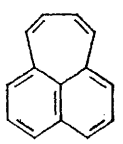
By S. O'Brien and D. C. C. Smith.

A new synthesis of 1-thiaphenalene (I), and syntheses of its hitherto unknown oxygen (II) and nitrogen (III) analogue, are described. Also substituted derivatives of 1-oxaphenalene, and other compounds having the ring systems (II) and (III), are prepared.

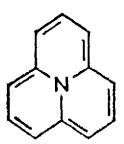
Current interest in *peri*-condensed aromatic compounds led us to devise syntheses of compounds having the tricyclic nuclei (I), (II), and (III). These heterocyclic compounds are structurally related to phenalene (IV), a hydrocarbon which forms salts with strong bases, analogously to indene.[1] Hence there are grounds for expecting that compounds



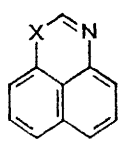
(I : X = S)
(II : X = O)
(III : X = NH)
(IV : X = CH_2)



(V)



(VI)



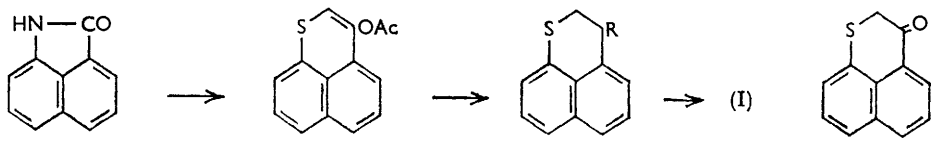
(VII : X = NH)
(VIII : X = S)
(IX : X = O)

(I—III) might show some aromatic properties similar to those of benzothiophen, benzofuran, and indole, respectively. Compounds (I—III) are also heterocyclic analogues of pleiadiene (V),[2] possessing a ring system with fourteen π-electrons; and 1*H*-1-azaphenalene (III) is an isomer of the postulated aromatic structure (VI).[3]

Several heteroaromatic compounds having three *peri*-condensed six-membered rings are known, including derivatives of 1*H*-1,3-diazaphenalene (perimidine) (VII)[4] and

[1] Boekelheide and Larrabee, *J. Amer. Chem. Soc.*, 1950, **72**, 1245; Reid, *Chem. and Ind.*, 1956, 1504.
[2] Boekelheide and Vick, *J. Amer. Chem. Soc.*, 1956, **78**, 653.
[3] Windgassen, Saunders, and Boekelheide, *J. Amer. Chem. Soc.*, 1959, **81**, 1459.
[4] Sachs, *Annalen*, 1909, **365**, 53; Richmond in Allen, "Six-Membered Heterocyclic Nitrogen Compounds with Three Condensed Rings," Interscience Publ. Inc., New York, 1958, Chapter 8.

naphtho[1,8-*de*]-1,3-thiazine (VIII) [5] and -1,3-oxazine (IX).[6] The only known examples having a single hetero-atom are 1-thiaphenalene (naphtho[1,8-*bc*]thiapyran) (I) and its 9-chloro- [7] and 3-acetoxy-derivative (XI).[8] Neither of the existing methods of making 1-thiaphenalene is satisfactory,[7,8] and since 3-acetoxy-1-thiaphenalene is readily prepared

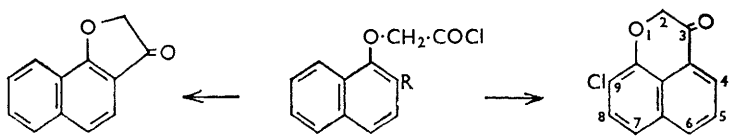


(X) (XI) (XII: R = OH) (XIII: R = Cl) (XIV)

from naphthastyril (X) [8] it seemed to offer a good route to 1-thiaphenalene; in the present work, it was converted into 1-thiaphenalene in 89% yield. Combined hydrolysis and reduction of 3-acetoxy-1-thiaphenalene (XI) with sodium borohydride gave 2,3-dihydro-1-thiaphenalen-3-ol (XII), without losses due to oxidative coupling of the intermediate ketone (XIV) which is known to occur very readily in alkaline solution.[8] Phosphorus pentachloride converted the alcohol (XII) into the chloro-compound (XIII), from which thiaphenalene was obtained by warm ethanolic potassium hydroxide.

In the hope of preparing 3-alkyl derivatives of 1-thiaphenalene, the acetate (XI) was cleaved by means of lithium aluminium hydride to the ketone (XIV), which despite its crystallisation as the ketonic tautomer failed to add methylmagnesium iodide and formed a magnesium enolate from which on hydrolysis the ketone (XIV) was recovered.

Of the analogous oxygen heterocycle, 1-oxaphenalene (II), only its benzo-derivatives are known.* Benzo[*kl*]xanthen has been isolated from coal tar,[9] and this compound,[10] its 10-hydroxy-derivative,[11] and naphtho[3,2,1-*kl*]xanthen (ceroxene) [12] have been synthesised. We accordingly explored synthetic routes to 1-oxaphenalene itself. Cyclisation of 2-chloro-1-naphthyloxyacetyl chloride (XVII) appeared promising. Ingham *et al.*[13] found that the acid chloride unsubstituted at position 2 (XVI) was cyclised by aluminium chloride, and the product was later proved to be 2,3-dihydronaphtho[1,2-*b*]-



(XV) (XVI: R = H) (XVII: R = Cl) (XVIII)

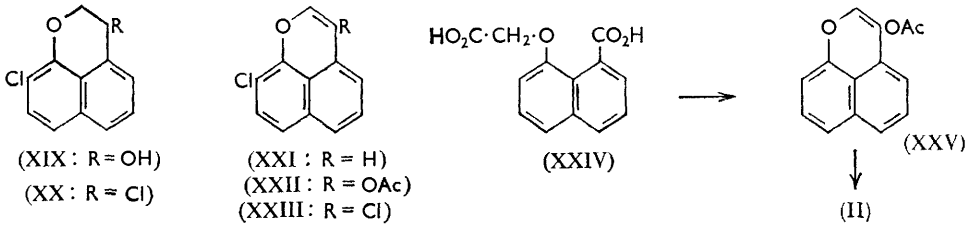
furan-3-one (XV) by an independent synthesis.[14] A blocking group in the *ortho*-position is therefore necessary to ensure *peri*-cyclisation. Treatment of 2-chloro-1-naphthol with sodium chloroacetate in alkali gave only small yields of 2-chloro-1-naphthyloxyacetic acid,

* [*Added in proof.*] A naturally occurring and some synthetic derivatives of 1-oxaphenalene have been described recently (Comin, Gonçalves de Lima, Grant, Jackman, and Prelog, *Helv. Chim. Acta*, 1963, **46**, 409.

[5] Bogert and Bartlett, *J. Amer. Chem. Soc.*, 1931, **53**, 4046; Joy and Bogert, *J. Org. Chem.*, 1936, **1**, 236.
[6] Fichter and Kühnel, *Ber.*, 1909, **42**, 4748.
[7] Desai, Rao, and Tilak, *Chem. and Ind.*, 1957, 464.
[8] Friedländer and Woroshzow, *Annalen*, 1912, **388**, 1.
[9] Kruber, *Ber.*, 1937, **70**, 1556.
[10] Orchin, *J. Amer. Chem. Soc.*, 1948, **70**, 495.
[11] Schimmelschmidt, *Annalen*, 1950, **566**, 184.
[12] Decker, *Annalen*, 1906, **348**, 210.
[13] Ingham, Stephen, and Timpe, *J.*, 1931, 895.
[14] Anand, *Proc. Indian Acad. Sci.*, 1948, **28**, *A*, 160.

probably owing to steric hindrance; also sodium 2-chloro-1-naphthyl oxide failed to react with chloroacetal, probably for the same reason. However, this sodio-derivative reacts smoothly with the more reactive ethyl bromoacetate, affording ethyl 2-chloro-1-naphthyloxyacetate. This was hydrolysed to the free acid and converted into the acid chloride (XVII), which was smoothly cyclised by aluminium chloride to 9-chloro-2,3-dihydro-1-oxaphenalen-3-one (XVIII). Reduction of this with sodium borohydride gave the alcohol (XIX), which with phosphorus pentachloride gave 3,9-dichloro-2,3-dihydro-1-oxaphenalene (XX). In refluxing ethanolic potassium hydroxide this compound gave 9-chloro-1-oxaphenalene (XXI). Other derivatives of 1-oxaphenalene can be prepared from the ketone (XVIII): with acetic anhydride and sodium acetate, 3-acetoxy-9-chloro-1-oxaphenalene (XXII) was formed, and with phosphorus pentachloride 3,9-dichloro-1-oxaphenalene (XXIII). The ketone (XVIII) was recovered unchanged after treatment with methylmagnesium iodide or methyl-lithium; presumably, like its sulphur analogue (XIV), it is converted into a metal enolate.

The parent 1-oxaphenalene (II) was obtained by a route parallel to that described above for 1-thiaphenalene. 8-Hydroxy-1-naphthoic acid lactone, on treatment with alkali and sodium chloroacetate, afforded the diacid (XXIV). This with acetic anhydride and sodium acetate, gave 3-acetoxy-1-oxaphenalene (XXV), which was converted, by steps described for the chloro-compound (XXII), into 1-oxaphenalene (II).



(XIX: R = OH)
(XX: R = Cl)

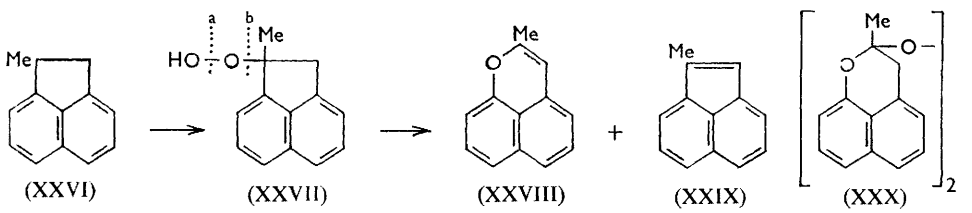
(XXI: R = H)
(XXII: R = OAc)
(XXIII: R = Cl)

(XXIV)

(XXV)

(II)

Another possible approach was from acenaphthene derivatives, by ring-expansion with the introduction of oxygen. 1-Methylacenaphthene (XXVI) was autoxidised readily, and the hydroperoxide (probably mainly XXVII) was precipitated as its sodium salt by means of concentrated aqueous sodium hydroxide. With acetic acid, containing a catalytic amount of perchloric acid, this hydroperoxide decomposed giving both 2-methyl-1-oxaphenalene (XXVIII) and 2-methylacenaphthylene (XXIX), that presumably result by heterolysis of the hydroperoxide (XXVII) at " a " and " b," respectively. An analogous hydroperoxide might be produced by addition of hydrogen peroxide to the reactive hydrocarbon acenaphthylene; if such addition is brought about in the presence of perchloric acid, immediate rearrangement to a derivative of 1-oxaphenalene could be expected. With acenaphthylene itself, the only product isolated was a small yield of *cis*-acenaphthene-



(XXVI)

(XXVII)

(XXVIII)

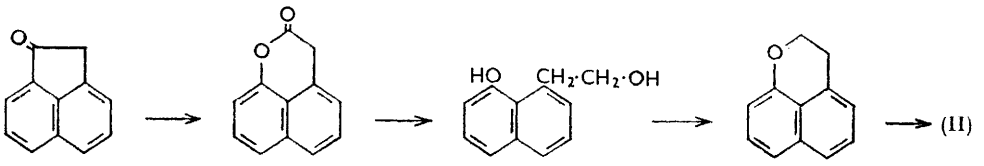
(XXIX)

(XXX)

1,2-diol. In contrast, 1-methylacenaphthylene (XXIX) reacted rapidly with hydrogen peroxide and perchloric acid in acetic acid, giving an oil containing active oxygen, and having the ultraviolet spectrum characteristic of 1-naphthol and its ethers. The main product was not further characterised, but a small amount of the symmetrical peroxide

(XXX) was isolated. Treibs and Schöllner [15] have reported the formation of 4,5-dihydrobenzo[*kl*]xanthen by a similar rearrangement of the hydroperoxide derived from 1,2,3,10b-tetrahydrofluoranthene.

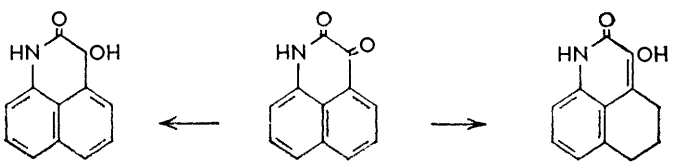
Another possible approach is by a ring expansion of acenaphthenone (XXXI). Oxidation of this ketone by peracetic acid with toluene-*p*-sulphonic acid as a catalyst, or by trifluoroperacetic acid, afforded a crystalline mixture containing unchanged ketone (XXXI) and 8-hydroxy-1-naphthylacetic acid lactone (XXXII). Separation proved difficult, so



(XXXI) (XXXII) (XXXIII) (XXXIV)

the mixture was reduced with lithium aluminium hydride to acenaphthenol and 2-(8-hydroxy-1-naphthyl)ethanol (XXXIII) which were easily separated. The diol (XXXIII), on treatment successively with phosphorus tribromide and with potassium carbonate, was cyclised to 2,3-dihydro-1-oxaphenalene (XXXIV). Attempts to dehydrogenate this ether with chloranil were unsuccessful, but when it was sublimed through heated palladium–charcoal it yielded some 1-oxaphenalene.

Though 1*H*-1-azaphenalene (III) has not previously been reported, its benzo-derivative, 7*H*-benz[*kl*]acridine, has been made.[16] The compound (XXXVI) seemed to offer a possible



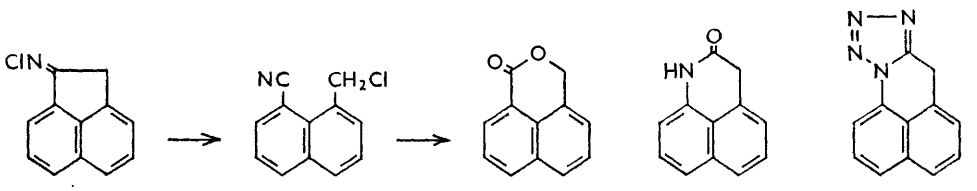
(XXXV) (XXXVI) (XXXVII)

starting point for the synthesis of 1*H*-1-azaphenalene. It was prepared by ring-closure of *N*-1-naphthyl-*N*-toluene-*p*-sulphonyloxamoyl chloride.[17] We confirmed its structure by oxidation to naphthastyril (X) with hydrogen peroxide in alkali. The compound (XXXVI) was subjected to various reducing agents, of which only two afforded crystalline reduction products: hydrogenation catalysed by perchloric acid gave 2,4,5,6-tetrahydro-3-hydroxy-1*H*-benzo[*de*]quinolin-2-one (XXXVII), a compound previously synthesised by another route.[18] Reduction with zinc and acetic acid afforded a dihydro-product, probably (XXXV). Reduction with lithium aluminium hydride or with sodium borohydride gave basic oils whose ultraviolet spectra resembled that of 1-naphthylamine, but which darkened rapidly in air.

An alternative approach to this ring system would be by ring-enlargement of acenaphthenone (XXXI), with the introduction of nitrogen. The oxime of this ketone, when treated with phosphorus pentachloride in the hope of inducing a Beckmann rearrangement, afforded instead crystalline *N*-chloro-1-acenaphtheneimine (XXXVIII). This showed an infrared band at 1750m cm.$^{-1}$ due to the C=N vibration. The exceptional strength and position of this band are attributable to the influence of both the chlorine and

[15] Treibs and Schöllner, *Chem. Ber.*, 1961, **94**, 42.
[16] Waldmann and Back, *Annalen*, 1940, **545**, 52.
[17] Schirmacher and Renn, U.S.P. 1,698,894/1929; *Chem. Abs.*, 1929, **23**, 1143.
[18] Uhle, Vernick, and Schmir, *J. Amer. Chem. Soc.*, 1955, **77**, 3334.

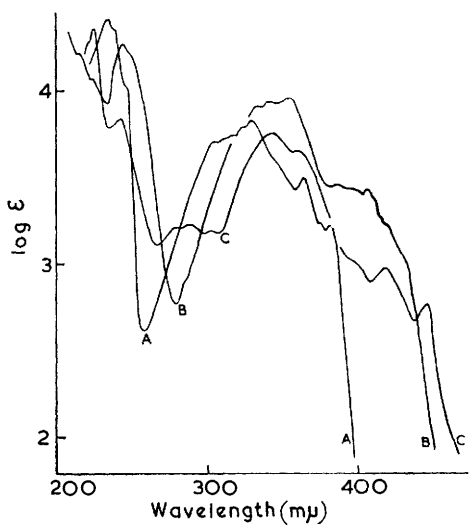
the five-membered ring. An analogous chloramine has been obtained from 2-nitrofluorenone oxime.[19] The structure of the chloramine (XXXVIII) is confirmed by its rearrangement in acetic acid: a mixture resulted, from which 8-chloromethyl-1-naphthonitrile (XXXIX) was isolated. This, on prolonged saponification, afforded 1,8-naphthalide (XL).



(XXXVIII) (XXXIX) (XL) (XLI) (XLII)

The Schmidt reaction, with hydrazoic acid, is reported to give only tar with acenaphthenone.[20] On reinvestigation, we find that both the lactam (XLI) and the tetrazole (XLII) can be isolated from the crude product by sublimation and chromatography. On reduction of the lactam (XLI) with lithium aluminium hydride only green amorphous products were obtained.

Some olefins react with hydrazoic acid.[21] With acenaphthylene we found rapid liberation of nitrogen and, when the amorphous product was sublimed or extracted with pentane, yellow crystals of 1*H*-1-azaphenalene (III) were obtained. This compound rapidly becomes green and then black in air, but can be stored unchanged in a vacuum. Its solutions in ether are unstable, rapidly depositing an insoluble brown polymer. Its ultraviolet spectrum is similar to those of 1-oxa- and 1-thia-phenalene, with far more absorption at longer wavelengths than for the isomers, carbazole, dibenzofuran, and dibenzothiophen, respectively (see the annexed figure).

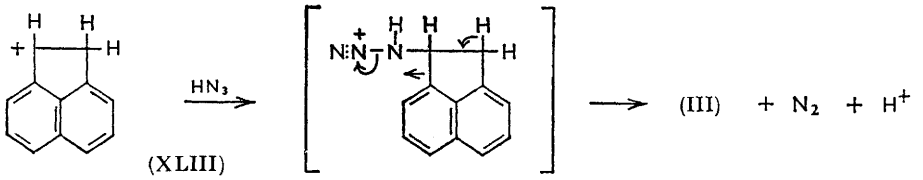


Absorption spectra of (A) 1-oxaphenalene, (B) 1-thiaphenalene, and (C) 1*H*-1-azaphenalene in ethanol.

In view of the instability of the 1*H*-1-azaphenalene, once isolated, the failure at the last stage of the previous synthetic approaches described in this paper is hardly surprising.

[19] Moore and Huntress, *J. Amer. Chem. Soc.*, 1927, **49**, 2618; Nunn, Schofield, and Theobald, *J.*, 1952, 2797.
[20] Edwards and Petrow, *J.*, 1948, 1713.
[21] Wolff in Adams's "Organic Reactions," Wiley, New York, 1946, Vol. III, Chapter 8.

The Schmidt reactions of acenaphthylene can be formulated as beginning with the carbonium ion (XLIII).



Experimental

Naphthastyril (X) was prepared by Karishinin and Kustol's method.[22] It was converted into 8-mercapto-1-naphthoic acid lactone, thence into 8-carboxy-1-naphthylthioacetic acid, and by cyclisation thereof into 3-acetoxy-1-thiaphenalene (XI) as described by Friedländer and Woroshzow.[8]

2,3-*Dihydro*-1-*thiaphenalen*-3-*ol* (XII).—3-Acetoxy-1-thiaphenalene (XI) (1·06 g.) was taken up in boiling methanol (100 c.c.), and mixed successively with potassium borohydride (1 g.), dissolved in water (50 c.c.), and aqueous N-sodium hydroxide (100 c.c.). The mixture was boiled for 1 hr., the methanol being allowed to distil gradually. The residue was cooled and extracted with ether. The extract was washed with brine and concentrated, leaving a glass which crystallised. This was extracted twice with boiling light petroleum (b. p. 60—80°), leaving a black residue which was discarded. The extracts, on concentration and cooling, deposited 2,3-*dihydro*-1-*thiaphenalen*-3-*ol* as brownish prisms, m. p. 70—73° (0·84 g.), $\lambda_{max.}$ 224, 242, 313 mμ (ε 29,400, 9800, 6900), shoulder 320 mμ (ε 6300) (Found: C, 71·55; H, 4·95. $C_{12}H_{10}OS$ requires C, 71·3; H, 5·0%).

3-*Chloro*-2,3-*dihydro*-1-*thiaphenalene* (XIII).—2,3-Dihydro-1-thiaphenalen-3-ol (139 mg.) in dry benzene (50 c.c.) was treated with phosphorus pentachloride (174 mg.), warmed to the b. p. during 5 min., and set aside for 10 min., then filtered in benzene through neutralised alumina. The eluate was concentrated and the residue recrystallised from light petroleum (b. p. 60—80°), affording 3-*chloro*-2,3-*dihydro*-1-*thiaphenalene* as colourless needles (79 mg.), m. p. 70° (Found: C, 65·6; H, 4·0; Cl, 16·3. $C_{12}H_9ClS$ requires C, 65·3; H, 4·1; Cl, 16·1%).

1-*Thiaphenalene* (I).—2,3-Dihydro-1-thiaphenalen-3-ol (104 mg.) in dry benzene (20 c.c.) was treated with phosphorus pentachloride (133 mg.) and boiled under reflux for 10 min. The solvent was then removed *in vacuo*, and the residue was boiled with potassium hydroxide (1 g.) in ethanol (50 c.c.) for 1 hr. The mixture was then cooled, diluted with water, and extracted with benzene. The extract was filtered through neutralised alumina which was washed with benzene. Evaporation of the eluate afforded 1-thiaphenalene, (97 mg.) as light orange cubes, m. p. 120—122° (recrystallisation from aqueous methanol did not raise this m. p.), $\lambda_{max.}$ 248, 357, 407 mμ (ε 18,000, 8500, 2700), $\nu_{max.}$ (in CS_2) 1636 cm.$^{-1}$ (C=C) (Found: C, 77·7; H, 4·4. Calc. for $C_{12}H_8S$: C, 78·2; H, 4·4%).

2,3-*Dihydro*-1-*thiaphenalen*-3-*one* (XIV).—3-Acetoxy-1-thiaphenalene (50 mg.) in dry ether was added to a suspension of lithium aluminium hydride and stirred for 1 hr. The excess of reagent was destroyed with methanol, dilute hydrochloric acid added, and the organic layer separated, dried ($MgSO_4$), and evaporated to a green gum (40 mg.). This sublimed at 80°/0·05 mm., yielding 2,3-dihydro-1-thiaphenalen-3-one (20 mg.), pale yellow prisms [from light petroleum (b. p. 60—80°), m. p. 78—80°, $\lambda_{max.}$ 266, 323, 381 (ε 10,000, 2500, 1900), shoulder 336 mμ (ε 2300), $\nu_{max.}$ (in CS_2) 1684 cm.$^{-1}$ (C=O) (Found: C, 72·05; H, 4·35. Calc. for $C_{12}H_8OS$: C, 72·0; H, 4·0%).

Ethyl 2-*Chloro*-1-*naphthyloxyacetate*.—2-Chloro-1-naphthol (2·3 g.) was added to a solution prepared by dissolving sodium (0·3 g.) in methanol. The mixture resulting was evaporated to dryness *in vacuo*, and the sodium salt remaining was taken up in water-free benzene (30 c.c.), mixed with ethyl bromoacetate (1·8 c.c.), and boiled under reflux for 4 hr. After addition of more benzene the organic layer was washed with dilute aqueous sodium hydroxide and water, dried ($MgSO_4$), and concentrated to a brown liquid. Distillation *in vacuo* afforded *ethyl* 2-*chloro*-1-*naphthyloxyacetate* (3·0 g.), b. p. 106—108°/0·05 mm., n_D^{20} 1·5830 (Found: C, 63·2; H, 4·8. $C_{14}H_{13}ClO_3$ requires C, 63·4; H, 4·9%).

This ester (1 g.) and 10% aqueous sodium hydroxide were boiled for 40 min., giving the *acid*

[22] Karishinin and Kustol, *J. Gen. Chem.* (*U.S.S.R.*), 1959, 1898.

(0·86 g.), m. p. 133—135° (from benzene–light petroleum) (Found: C, 61·1; H, 4·2. $C_{12}H_9ClO_3$ requires C, 60·9; H, 3·8%).

2-*Chloro*-1-*naphthyloxyacetyl Chloride*.—The preceding acid (0·59 g.) and phosphorus pentachloride (0·52 g.) in water-free benzene (5 c.c.) were boiled under reflux for 10 min. After cooling, the solution was washed with aqueous sodium hydrogen carbonate, then concentrated, leaving the *acid chloride* (0·39 g.), m. p. 62—63° [from light petroleum (b. p. 60—80°)] (Found: C, 56·4; H, 3·3. $C_{12}H_8Cl_2O_2$ requires C, 56·5; H, 3·2%).

9-*Chloro*-2,3-*dihydro*-1-*oxaphenalen*-3-*one* (XIII).—2-Chloro-1-naphthyloxyacetic acid (6·6 g.) and phosphorus pentachloride (6·4 g.) in benzene (25 c.c.) were boiled under reflux for 30 min. Benzene and phosphorus oxychloride were then evaporated *in vacuo*, leaving a crude crystalline acid chloride. This was dissolved in benzene (75 c.c.), and treated with aluminium chloride (4·1 g.), portionwise with stirring, during 30 min. After a further 4 hr., the mixture was decomposed with ice and concentrated hydrochloric acid. The organic layer was separated, washed with water, concentrated to 20 c.c., and mixed with light petroleum (30 c.c.) (b. p. 60—80°). The solution deposited yellow 9-*chloro*-2,3-*dihydro*-1-*oxaphenalen*-3-*one* (3·3 g.). A portion, recrystallised from benzene–light petroleum (b. p. 80—100°), had m. p. 141—143°, $\lambda_{max.}$ 261, 339, 363, 381 mμ (ε 24,300, 2500, 3100, 3300), shoulder 399 mμ (ε 2200), $\nu_{max.}$ (in CS_2) 1702 cm.$^{-1}$ (C=O) (Found: C, 66·1; H, 3·35. $C_{12}H_7ClO_2$ requires C, 65·9; H, 3·2%).

3-*Acetoxy*-9-*chloro*-1-*oxaphenalene* (XXII).—9-Chloro-2,3-dihydro-1-oxaphenalen-3-one (100 mg.), fused sodium acetate (100 mg.), and acetic anhydride (5 c.c.) were boiled under reflux for 30 min., then poured into ice–water, and stirred for 30 min. The product was isolated with ether as red-brown crystals. These sublimed at 90—100°/0·01 mm. to give yellow 3-*acetoxy*-9-*chloro*-1-*oxaphenalene* (93 mg.). A portion, recrystallised from methanol, had m. p. 142—144°, $\lambda_{max.}$ 239, 313, 338 mμ (ε 36,000, 6300, 7700), shoulders 253, 364, 380 mμ (ε 16,400, 3400, 1650), $\nu_{max.}$ (in CS_2) 1663 cm.$^{-1}$ (C=C) (Found: C, 64·35; H, 3·5. $C_{14}H_9ClO_3$ requires C, 64·4; H, 3·5%).

3,9-*Dichloro*-1-*oxaphenalene* (XXIII).—9-Chloro-2,3-dihydro-3-oxo-1-oxaphenalene (100 mg.) and phosphorus pentachloride (120 mg.) in benzene (4 c.c.) were boiled under reflux for 10 min., then cooled and filtered through a column of neutral alumina. Benzene eluted a crystalline mixture of 3,3,9-trichloro-2,3-dihydro-1-oxaphenalene and 3,9-dichloro-1-oxaphenalene. A portion recrystallised from light petroleum had m. p. 80—100°, $\nu_{max.}$ (in CS_2) 1638 cm.$^{-1}$ (C=C) (Found: C, 55·8; H, 2·65. Calc. for $C_{12}H_7Cl_3O$,$C_{12}H_6Cl_2O$: C, 56·4; H, 2·5%). The mixture (17 mg.) was sublimed under nitrogen, through glass wool heated at 220°. The sublimate (15 mg.) recrystallised from light petroleum (b. p. 60—80°), giving 3,9-*dichloro*-1-*oxaphenalene*, slightly yellow needles, m. p. 132—134°, $\lambda_{max.}$ 240, 313, 337, 369, 387 mμ (ε 30,000, 6300, 6500, 2500, 1300), $\nu_{max.}$ (in CS_2) 1639 cm.$^{-1}$ (C=C) (Found: C, 61·1; H, 2·7. $C_{12}H_6Cl_2O$ requires C, 60·8; H, 2·5%).

9-*Chloro*-2,3-*dihydro*-1-*oxaphenalen*-3-*ol* (XIX).—9-Chloro-2,3-dihydro-1-oxaphenalen-3-one (100 mg.) was treated in warm methanol with potassium borohydride in dilute aqueous sodium hydroxide. The solution was set aside for 10 min., then diluted with water and extracted with ether. Evaporation of the extract afforded 9-*chloro*-2,3-*dihydro*-1-*oxaphenalen*-3-*ol* (99 mg.), prisms, m. p. 100—104° [from ether–light petroleum (b. p. 40—60°)], $\lambda_{max.}$ 233, 300, 332 mμ (ε 44,000, 5700, 2300) (Found: C, 65·45; H, 4·15. $C_{12}H_9ClO_2$ requires C, 65·4; H, 4·1%).

3,9-*Dichloro*-2,3-*dihydro*-1-*oxaphenalene* (XX).—9-Chloro-2,3-dihydro-1-oxaphenalen-3-ol (100 mg.) and phosphorus pentachloride (123 mg.) in benzene (5 c.c.) were boiled under reflux for 5 min., then cooled and filtered through a column of neutral alumina. Benzene eluted 3,9-*dichloro*-2,3-*dihydro*-1-*oxaphenalene* (83 mg.), that recrystallised from light petroleum (b. p. 60—80°) as prisms, m. p. 86—88° (Found: C, 60·45; H, 3·5. $C_{12}H_8Cl_2O$ requires C, 60·4; H, 3·35%).

9-*Chloro*-1-*oxaphenalene* (XXI).—3,9-Dichloro-2,3-dihydro-1-oxaphenalene (83 mg.) was boiled under reflux with 1% ethanolic potassium hydroxide solution for 1 hr. The mixture was diluted with water and extracted with benzene. The extract was filtered through a column of neutral alumina, and benzene eluted 9-*chloro*-1-*oxaphenalene* (63 mg.) that recrystallised from methanol as pale yellow prisms, m. p. 66—68°, $\lambda_{max.}$ 240, 312, 337, 382 mμ (ε 41,000, 6400, 7900, 1700), $\lambda_{sh.}$ 363 mμ (ε 3600), $\nu_{max.}$ (in CS_2) 1642 cm.$^{-1}$ (C=C) (Found: C, 70·85; H, 3·4. $C_{12}H_7ClO$ requires C, 71·1; H, 3·45%).

8-*Carboxy*-1-*naphthyloxyacetic Acid* (XXIV).—The lactone of 8-hydroxy-1-naphthoic acid (2·9 g.) was dissolved, with warming, in a solution of sodium hydroxide (11·5 g.) in water (50 c.c.). Chloroacetic acid (16·2 g.) was added, and the mixture boiled under reflux for 4 hr., with further addition of alkali at intervals to keep it alkaline. After cooling, the solution was acidified with concentrated hydrochloric acid, that precipitated crude 8-*carboxy*-1-*naphthyloxyacetic acid*. This was washed with water and recrystallised twice from methanol, forming colourless crystals (1·3 g.), m. p. 272—274° (Found: C, 63·05; H, 4·3. $C_{13}H_{10}O_5$ requires C, 63·4; H, 4·1%).

3-*Acetoxy*-1-*oxaphenalene* (XXV).—8-Carboxy-1-naphthyloxyacetic acid (1·1 g.) was dissolved in a solution of potassium hydroxide (0·56 g.) in methanol (10 c.c.). The solution was evaporated *in vacuo* to dryness, and the residue boiled with acetic anhydride (25 c.c.) and potassium acetate for 30 min., poured into ice–water, stirred for 30 min., and extracted with ether. The extract was washed with sodium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated. The residue recrystallised from methanol, giving 3-*acetoxy*-1-*oxaphenalene* (0·50 g.), yellow prisms, m. p. 91—94°, $\lambda_{max.}$ 235, 335, 368 mμ (ε 24,600, 7760, 3470), shoulders 312, 385 mμ (ε 6100, 1800), $\nu_{max.}$ (in CS_2) 1665 cm.$^{-1}$ (C=C) (Found: C, 74·55; H, 4·5. $C_{14}H_{10}O_3$ requires C, 74·3; H, 4·5%).

1-*Oxaphenalene* (II).—3-Acetoxy-1-oxaphenalene (400 mg.) in methanol was treated with a solution of potassium borohydride in dilute aqueous sodium hydroxide. After 10 min., water was added, and the product was isolated with ether as a yellow glass (300 mg.). This was boiled under reflux with a solution of phosphorus pentachloride (420 mg.) in benzene (5 c.c.) for 5 min. The resulting solution was filtered through a column of neutral alumina. Benzene eluted a yellow gum (250 mg.) which crystallised. This was boiled under reflux with 1% ethanolic potassium hydroxide (25 c.c.) for 1 hr. The mixture was diluted with water and extracted with benzene. The extract was filtered through a column of neutral alumina, and benzene eluted 1-*oxaphenalene* (162 mg.), which crystallised. Sublimation at 30°/0·05 mm. gave an almost colourless product, m. p. 44—54°, $\lambda_{sh.}$ 237, 333, 367 mμ (ε 27,000, 7800, 3300), 315, 384 mμ (ε 6300, 1750), $\nu_{max.}$ (in CS_2) 1643 cm.$^{-1}$ (C=C) (Found: C, 85·35; H, 4·8. $C_{12}H_8O$ requires C, 85·7; H, 4·8%).

Autoxidation of 1-*Methylacenaphthene* (XXVI).—1-Methylacenaphthene (1·8 g.) and benzoyl peroxide (6 mg.) were aerated at 60—70°. Samples were removed at intervals, weighed, and examined for active oxygen content as follows. The sample, 2 c.c. of a mixture of acetic acid (3 parts) and chloroform (2 parts), and saturated aqueous potassium iodide (8 drops) were kept for 5 min., then diluted with water and titrated with 0·05N-sodium thiosulphate (starch). A control determination to measure aerial oxidation of the aqueous hydriodic acid gave titres of less than 0·02 c.c.:

Time (hr.)	2	3	4	5	6
Sample weight (mg.)	24·6	29·9	35·7	35·6	36·1
Titre (c.c.)	0·289	0·562	0·854	0·999	1·145
Hydroperoxide (as $C_{13}H_{12}O_2$) (%)	6·3	10·0	14·2	15·0	16·8

The product from 6 hours' aeration was diluted with pentane and triturated with concentrated aqueous sodium hydroxide at 0°. After 5 min., the liquid was decanted and the crystalline residue washed with pentane. The residue was then mixed with water, liberating a colourless oil. This was isolated by extraction with ether, drying (Na_2SO_4), and removal of solvent, as a colourless viscous oil (364 mg.), $\lambda_{max.}$ 276, 285 mμ (ε 7000, 7600) (Found: active O, 6·73. $C_{13}H_{12}O_2$ requires active O, 7·91%).

Action of Perchloric Acid on the Hydroperoxide (XXVII).—The hydroperoxide (211 mg.) in acetic acid (20 c.c.) was treated with a solution prepared by dissolving 60% aqueous perchloric acid (1 drop) in acetic acid (10 c.c.). The reaction was followed spectrophotometrically and was almost complete after 15 min. After 40 min. at room temperature, when the solution had become green, it was diluted with water and extracted with ether. The organic layer was washed with water, dried (Na_2SO_4), and evaporated, leaving a green oil (180 mg.). This oil was extracted with pentane (blue residue, 11 mg.) and chromatographed on neutral alumina. Pentane eluted 1-methylacenaphthylene mixed with some 2-methyl-1-oxaphenalene (41 mg.) This material was rechromatographed; the first fraction gave an orange 2-methylacenaphthylene picrate, m. p. 165—179°. Ether (2%) in pentane eluted 2-*methyl*-1-*oxaphenalene* (40 mg.), which crystallised on removal of solvent. It recrystallised from methanol at 0° as pale cream prisms, m. p. 43—44°, $\lambda_{max.}$ 239, 332, 365, 384 mμ (ε 37,000, 10,400, 5100,

3200), $\nu_{max.}$ (in CS_2) 1670 cm.$^{-1}$ (C=C) (Found: C, 85·3; H, 5·5. $C_{13}H_{10}O$ requires C, 85·7; H, 5·5%).

Action of Hydrogen Peroxide and Perchloric acid on Acenaphthylene.—Acenaphthylene (205 mg.) in glacial acetic acid (5 c.c.) and 30% aqueous hydrogen peroxide (5 c.c.) was treated with 1% perchloric acid in acetic acid (5 c.c.). The mixture was kept at room temperature for 3 days, then poured into water and extracted with ether. The extract was washed with aqueous potassium hydrogen carbonate, then concentrated, giving a solid residue (112 mg.). This was recrystallised first from benzene, then from methanol–benzene, giving *cis*-acenaphthene-1,2-diol [23] (13 mg.), m. p. 208—209° (Found: C, 77·5; H, 5·45. Calc. for $C_{12}H_{10}O_2$: C, 77·4; H, 5·4%).

Action of Hydrogen Peroxide and Perchloric Acid on 1-Methylacenaphthylene.—1-Methylacenaphthen-1-ol (which is rapidly dehydrated to 1-methylacenaphthylene in acetic acid) (205 mg.) [24] in acetic acid (5 c.c.) and 30% aqueous hydrogen peroxide (10 c.c.) was treated with a solution prepared by dissolving 60% aqueous perchloric acid (1 c.c.) in acetic acid (100 c.c.). After 30 min. at room temperature the yellow colour due to 1-methylacenaphthylene had disappeared, and the mixture was poured into water and extracted with ether. The extract was washed with potassium hydrogen carbonate solution, dried (Na_2SO_4), and evaporated to a viscous colourless oil (237 mg.). This had an ultraviolet spectrum almost identical with that of 1-naphthol and contained active oxygen. This product was boiled with picric acid in benzene, then passed through a column of alumina. Benzene eluted a pale yellow oil which crystallised on contact with ethanol. This was recrystallised from ethanol, giving *bis*-(2,3-*dihydro*-2-*methyl*-1-*oxaphenalen*-2-*yl*) *peroxide* as colourless prisms (15 mg.), m. p. 162—168°, $\lambda_{max.}$ 296, 310, 324 mμ (ε 12,700, 7900, 5600), $\nu_{max.}$ (in CS_2) 1036, 1082, 1114, 1152 cm.$^{-1}$ (ketal C–O) (Found: C, 78·65; H, 5·8. $C_{26}H_{22}O_4$ requires C, 78·4; H, 5·6%).

Oxidation of Acenaphthenone.—Method (a). Acenaphthenone (1 g.), toluene-*p*-sulphonic acid hydrate (1 g.), and peracetic acid in acetic acid (60 c.c.; containing 1·48 g./100 c.c. of active oxygen), were mixed and kept at room temperature for 3 days, then poured into dilute aqueous sodium hydrogen sulphite and extracted with benzene. The extract was washed with aqueous sodium hydrogen carbonate, concentrated, and filtered through a column of Florex (60—100 mesh). Benzene eluted a mixture of acenaphthenone and 8-hydroxy-1-naphthylacetic acid lactone (500 mg.). Recrystallised from benzene–light petroleum (b. p. 60—80°), the latter mixture had m. p. 95—97°, $\nu_{max.}$ (in CS_2) 1722 (acenaphthenone, C=O), and 1780 cm.$^{-1}$ (lactone, C=O).

Method (b). Hydrogen peroxide (80%; 1·3 c.c.) and methylene dichloride (10 c.c.) were cooled at 0°, stirred, and treated with trifluoroacetic anhydride (10 c.c.). The mixture was stirred until it became homogeneous (1 hr.), then it was added slowly to a stirred mixture of acenaphthenone (4 g.), disodium hydrogen phosphate (18 g.), and methylene dichloride (30 c.c.). After the initial exothermic reaction had subsided, the mixture was stirred for 3 hr., then filtered. The organic layer in the filtrate was separated, washed with aqueous sodium hydrogen carbonate, concentrated, and filtered through a column of Florex (60—100 mesh). Benzene eluted a mixture of acenaphthenone and the lactone (2·24 g.), m. p. 100—108° (Found: C, 80·8; H, 4·65. Calc. for 1 : 1 $C_{12}H_8O$–$C_{12}H_8O_2$: C, 82·0; H, 4·1%).

2-(8-*Hydroxy*-1-*naphthyl*)*ethanol* (XXXIII).—The mixture of acenaphthenone and lactone (XXXII) obtained by method (*b*) above (300 mg.) was taken up in ether and stirred with a suspension of lithium aluminium hydride for 3 hr. The excess of hydride was destroyed with methanol, and the solution resulting was shaken with dilute sulphuric acid. The organic layer was separated and extracted with dilute aqueous potassium hydroxide. The ether layer remaining gave acenaphthenol (230 mg.) on evaporation. The alkaline extract was acidified with hydrochloric acid and extracted with ether. The extract was dried ($MgSO_4$) and evaporated, giving 2-(8-*hydroxy*-1-*naphthyl*)*ethanol* (46 mg.), whose ethanolic ferric chloride reaction was dark red; this had m. p. 134—136° (from benzene), $\lambda_{max.}$ 301, 315, 329 mμ (ε 6800, 5600, 4200) (Found: C, 76·4; H, 6·5. $C_{12}H_{12}O_2$ requires C, 76·6; H, 6·4%).

2,3-*Dihydro*-1-*oxaphenalene* (XXXIV).—The diol (XXXIII) (50 mg.) was boiled under reflux with a solution of phosphorus tribromide (350 mg.) in benzene (10 c.c.) for 15 min., then poured on ice. The organic layer was separated, washed with potassium hydrogen carbonate solution, dried ($MgSO_4$), and concentrated. The residue was taken up in acetone and shaken

[23] Jack and Rule, *J.*, 1938, 188.
[24] O'Brien and Smith, unpublished work.

with solid potassium carbonate for 16 hr. The solids were filtered off, the acetone was evaporated, and the residue was taken up in ether, washed, dried ($MgSO_4$), and evaporated, leaving 2,3-dihydro-1-oxaphenalene (23 mg.) as a colourless oil, n_D^{20} 1·6330, $\lambda_{max.}$ 299, 311, 327 mμ (ε 5500, 4100, 2600). Its *picrate*, prepared in, and recrystallised from, ethanol, had m. p. 139—142° (Found: C, 53·8; H, 3·35; N, 10·8. $C_{18}H_{13}N_3O_8$ requires C, 54·1; H, 3·3; N, 10·5%).

Dehydrogenation of 2,3-*Dihydro*-1-*oxaphenalene*.—2,3-Dihydro-1-oxaphenalene (10 mg.) was sublimed at atmospheric pressure in a stream of dry nitrogen, through a layer of 10% palladium–charcoal at 350°. The catalyst was maintained at this temperature for 30 min. A negligible quantity (0·03 mg.) of material sublimed through the catalyst on to the cold part of the tube; this had an ultraviolet absorption spectrum characteristic of the starting material. Extraction of the catalyst with chloroform afforded a wax (2 mg.) having the same ultraviolet absorption spectrum as authentic 1-oxaphenalene.

1,8-*Naphthisatin* (XXXVI).—*N*-Toluene-*p*-sulphonyl-1-naphthylamine (8·9 g.) was mixed with a solution prepared by dissolving sodium (0·76 g.) in methanol (60 c.c.), and the whole was evaporated to dryness. The sodium salt thus obtained was boiled in dry benzene (100 c.c.) with oxalyl chloride (3·6 c.c.) for 3 hr. under nitrogen. The mixture was then filtered and concentrated to a pale yellow glass. This was stirred in benzene (50 c.c.) with aluminium chloride (4·8 g.) for 6 hr., then treated with dilute hydrochloric acid and chloroform. Solids were filtered off and washed with chloroform. The organic layer in the combined filtrate and washings was concentrated, leaving a semi-solid residue. This was extracted with benzene, leaving a residue of 1,8-naphthisatin (XXXVI) (320 mg.), m. p. 295—300° (from acetic acid), $\lambda_{max.}$ 248, 271, 362, 420 mμ (ε 15,300, 17,000, 3400, 7900) $\lambda_{sh.}$ 242, 264, 296 mμ (ε 14,900, 15,000, 13,300), $\nu_{max.}$ (in Nujol) 1671 (C=O), 3150 cm.$^{-1}$ (N–H) (Found: C, 72·75; H, 3·55. Calc. for $C_{12}H_7NO_2$: C, 73·1; H, 3·6%).

Degradation of 1,8-*Naphthisatin with Alkaline Hydrogen Peroxide*.—1,8-Naphthisatin (16 mg.) was dissolved in warm 10% aqueous sodium hydroxide (3 c.c.), then cooled and treated with 6% aqueous hydrogen peroxide (5 c.c.). After 1 hr., the mixture was acidified with hydrochloric acid, boiled briefly, and allowed to cool. The solid was filtered off and sublimed at 100—110°/0·05 mm., giving naphthastyril (13 mg.), m. p. 170—172°, $\lambda_{max.}$ 251, 273, 322, 338, 363 mμ (ε 22,100, 6100, 2900, 4500, 3900).

Reduction of 1,8-*Naphthisatin* (XXXVI).—(*a*) *Hydrogenation*. 1,8-Naphthisatin (30 mg.) was dissolved in methanol (20 c.c.) containing 60% aqueous perchloric acid (0·1 c.c.) and hydrogenated with 50 mg. of 10% palladium–charcoal. Initial uptake of hydrogen was rapid (9 c.c.) and after 30 min. the catalyst was filtered off, water added, and the filtrate extracted with benzene. The extract was washed and concentrated, giving a pale green crystalline residue (20 mg.). This sublimed at 120—130°/0·05 mm., giving 2,4,5,6-tetrahydro-3-hydroxy-1*H*-benzo[*de*]quinolin-2-one (XXXVII), m. p. 215—222°, $\lambda_{max.}$ 225, 294, 317, 330 mμ (ε 38,000, 8700, 9500, 7800), $\nu_{max.}$ (in Nujol) 1665 (C=O), 3280, 3380 cm.$^{-1}$ (NH, OH), giving a dark green colour with ferric chloride and a yellow solution in N-sodium hydroxide (Found: C, 71·65; H, 5·4. Calc. for $C_{12}H_{11}NO_2$: C, 71·6; H, 5·5%).

(*b*) *With zinc and acetic acid*. 1,8-Naphthisatin (25 mg.), suspended in ethanol (10 c.c.) and acetic acid (1 c.c.), was shaken with zinc dust (250 mg.) for 30 min. By this time the yellow colour had faded. The solids were filtered off, and the filtrate was diluted with water and extracted with ethyl acetate. Concentration of the extract gave yellow crystals (21 mg.) that recrystallised from benzene giving 2,3-*dihydro*-3-*hydroxy*-1H-*benzo*[de]*quinolin*-2-*one* (XXXV), m. p. 292—300°, $\lambda_{max.}$ 271, 313, 422 mμ (ε 6500, 7200, 2300) $\lambda_{sh.}$ 225, 320, 336 mμ (ε 25,000, 6700, 5400), $\nu_{max.}$ (in Nujol) 1680 (C=O), 3200, 3400 cm.$^{-1}$ (NH, OH) (Found: C, 73·2; H, 4·55. $C_{12}H_9NO_2$ requires C, 72·4; H, 4·55%).

N-*Chloro*-1-*acenaphtheneimine* (XXXVIII).—Potassium acetate (10 g.) and hydroxylamine hydrochloride (7 g.) were dissolved separately in warm methanol and then mixed, cooled, and filtered. The filtrate (100 c.c.) and acenaphthenone (11·3 g.) were warmed on the steam-bath for 15 min., then cooled. The oxime was collected, washed with methanol, and recrystallised from methanol–ethyl acetate, forming pale yellow prisms (5·0 g.), m. p. 193—194° (Found: C, 78·4; H, 4·9; N, 7·4. Calc. for $C_{12}H_9NO$: C, 78·7; H, 4·95; N, 7·65%). With benzenesulphonyl chloride in pyridine it afforded a *benzenesulphonate*, needles (from ethyl acetate), m. p. 165—167° Found: C, 67·1; H, 4·1; N, 4·0. $C_{18}H_{13}NO_3S$ requires C, 66·9; H, 4·05; N, 4·3%).

Acenaphthenone oxime (1 g.) was boiled under reflux for 10 min. with a solution of phosphorus pentachloride (1·4 g.) in benzene (100 c.c.). The mixture was stirred with water, freed from solid, and separated into layers. The organic layer was washed with water and evaporated to a gum (1·0 g.). This was chromatographed on Florex in benzene; benzene eluted N-*chloro*-1-*acenaphtheneimine*, colourless crystals [from light petroleum (b. p. 60—80°)], (0·50 g.), m. p. 96—98°, $\lambda_{max.}$ 229, 303 mμ (ε 36,800, 8000), shoulders 293, 311, 347 mμ (ε 6400, 6300, 69), $\nu_{max.}$ (in CS_2) 1750 cm.$^{-1}$ (C=N) (Found: C, 71·0; H, 4·0. $C_{12}H_8ClN$ requires C, 71·4; H, 4·0%).

Action of Acid on N-*Chloro*-1-*acenaphtheneimine*.—The chloroimine (500 mg.) was boiled for 1 hr. with 70% acetic acid (50 c.c.), cooled, diluted with water, and extracted with benzene, yielding, after washing with sodium hydrogen carbonate solution and concentration, a crystalline residue (460 mg.). This was chromatographed on neutral alumina. Benzene eluted 8-*chloromethyl*-1-*naphthonitrile* (XXXIX) (65 mg.), needles [from light petroleum (b. p. 60—80°)], m. p. 96—97°, $\lambda_{max.}$ 228, 303 mμ (ε 36,500, 7700), shoulder 313 mμ (ε 6100), $\nu_{max.}$ (in Nujol) 2220 cm.$^{-1}$ (C≡N) (Found: C, 71·7; H, 3·9; N, 7·0. $C_{12}H_8ClN$ requires C, 71·4; H, 4·0; N, 7·0%).

Saponification of 8-*Chloromethyl*-1-*naphthonitrile*.—8-Chloromethyl-1-naphthonitrile (40 mg.) was boiled with 30% aqueous sodium hydroxide for 90 min. The mixture was cooled, diluted with water, and extracted with chloroform. This extract afforded a gum (23 mg.) still having the characteristic infrared absorption band of nitriles. The aqueous layer was acidified with hydrochloric acid and extracted with chloroform. This extract was washed, dried ($MgSO_4$), and concentrated, giving 1,8-naphthalide (XL) (9 mg.), m. p. 150—156° (from light petroleum), $\lambda_{max.}$ 240, 317, 328 (ε 14,500, 4900, 4800), identical with authentic 1,8-naphthalide.[25]

Schmidt Reaction of Acenaphthenone.—Acenaphthenone (2 g.) in chloroform (20 c.c.) was stirred with 1·0N-hydrazoic acid in chloroform (14 c.c.) at 40—45° and treated with concentrated sulphuric acid (4 c.c.) during 30 min. After a further 60 minutes' stirring, the mixture was diluted with aqueous ammonia and additional chloroform and filtered through kieselguhr. The organic layer, on concentration, gave a black glass (2·3 g.). This was treated with charcoal in boiling ethanol; filtration and evaporation gave a gum (1·5 g.), which was chromatographed in benzene on Florisil. The products eluted with benzene and benzene–chloroform were not characterised. Chloroform eluted the *tetrazole* (XLII) (250 mg.), m. p. 170—174° [from benzene–light petroleum (b. p. 80—100°)], obtained colourless on sublimation at 125—135°/0·05 mm.; it then had m. p. 174—175° (Found: C, 69·25; H, 3·6. $C_{12}H_8N_4$ requires C, 69·2; H, 3·9%). Methanol (5%) in chloroform eluted a fraction (310 mg.) which was rechromatographed on Florex: after the chloroform eluate had been discarded, methanol (5%) in chloroform eluted 8-*amino*-1-*naphthylacetic acid lactam* (XLI), that after crystallisation from benzene and sublimation at 130—140°/0·05 mm. had m. p. 196—199°, $\lambda_{max.}$ 238, 313 mμ (ε 23,300, 6700), shoulder 327 mμ (ε 5200), $\nu_{max.}$ (in Nujol) 1672 (C=O), 3180 cm.$^{-1}$ (NH) (Found: C, 78·7; H, 4·65. $C_{12}H_9NO$ requires C, 78·7; H, 4·95%).

1H-1-*Azaphenalene* (III).—Acenaphthylene (3 g.) and 0·8N-hydrazoic acid in chloroform (80 c.c.) were stirred with concentrated sulphuric acid (2 c.c.), and warmed to 50° under a reflux condenser. Above 30° there was a rapid evolution of nitrogen. The mixture was maintained at 50° with stirring for 30 min., then cooled to 0°, neutralised by saturated aqueous potassium hydrogen carbonate, and filtered through kieselguhr. The organic layer in the filtrate was dried ($MgSO_4$) and concentrated *in vacuo* without heating, leaving a green glass. This was extracted with boiling pentane (residue rejected), giving 1H-1-*azaphenalene* (0·24 g.) as yellow prisms, becoming green and then black within a few minutes. Extraction of deteriorated material with pentane once more gave a yellow product, and when recrystallised twice from pentane at −80° this (42 mg.) had m. p. 61—66°, $\lambda_{max.}$ 246, 346, 424, 449 mμ (ε 7900, 9200, 1400, 900), $\nu_{max.}$ (in CS_2) 1638 (C=C), 3552 cm.$^{-1}$ (NH) (Found: C, 86·4; H, 5·5; N, 7·5. $C_{12}H_9N$ requires C, 86·2; H, 5·4; N, 8·4%).

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[25] Fuson and Munn, *J. Amer. Chem. Soc.*, 1949, **71**, 1870.