812. *The Synthesis of* 3 : 4- *and* 5 : 6-*Benzophenanthridines.*

By B. Mills and K. Schofield.

1-*o*-Acylaminoarylnaphthalenes have been cyclised to give 5 : 6-benzophenanthridine and some of its mono- and di-methyl derivatives. Acyl derivatives of *trans*-2-1′-naphthyl*cyclo*hexylamine could not be so cyclised. Anils of 2-hydroxymethylene-1-tetralone were converted into tetra(?)hydro-1 : 2 : 8 : 9-dibenzacridine by hot formic acid. 3-Acetyl-4-phenyl- and -*o*-tolyl-quinoline were prepared.

1-Phenyl-, 1-*p*-tolyl-, and 1-*o*-tolyl-2-tetralone have been prepared from the related epoxides. The oximes of the first two of the ketones were converted into 1-phenyl- and 1-*p*-tolyl-2-naphthylamine, acyl derivatives of which have been cyclised to give 3 : 4-benzophenanthridines.

Neither 5 : 6-benzophenanthridine (I; R = R′ = R″ = H) nor any of its derivatives have previously been described, and little is known about the 3 : 4-benzophenanthridines (II; R = R′ = H).[1] We have attempted to synthesise examples of these tetracyclic compounds because of their relation to the stereochemically interesting 3 : 4-benzophenanthrenes.[2]

5 : 6-*Benzophenanthridines.*—Hollingsworth and Petrow[3] obtained tetrahydrophenanthridines by cyclising with hot formic acid the anils derived from 2-hydroxymethylene-*cyclo*hexanone and aniline, α- and β-naphthylamine, and 3-aminoacenaphthene. Although the reaction failed with substituted anilines there was no obvious reason why the alicyclic portion of the anil should not be varied, and by application to 2-phenyliminomethyl-1-tetralone (III) the method might have given 5 : 6-benzophenanthridine.

Von Auwers and Wiegand[4] described 2-phenyliminomethyl-1-tetralone as a yellow compound, m. p. 117—119°, but in following their method we obtained from the reaction between aniline and 2-hydroxymethylene-1-tetralone two distinct substances. One of these was orange (m. p. 76—78°) and one yellow (m. p. 132—135°), and examination suggests that they are merely polymorphic forms of (III). Their ultraviolet absorption spectra were substantially identical and their reactions the same (see Experimental section). The anils from 2-hydroxymethylene-1-tetralone and *o*- and *p*-toluidine. *p*-anisidine, and β-naphthylamine were obtained only as yellow forms.

With hot formic acid all of these anils gave as the only homogeneous product a poor yield of the same compound, which could be dehydrogenated to a cream-coloured substance,

[1] Allen, " Six-Membered Heterocyclic Nitrogen Compounds with Four Condensed Rings," Interscience Publ., New York, 1951, p. 139; Walker, *J. Amer. Chem. Soc.*, 1954, **76**, 3999.
[2] Newman and Wheatley, *J. Amer. Chem., Soc.*, 1948, **70**, 1913.
[3] Hollingsworth and Petrow, *J.*, 1948, 1537.
[4] Von Auwers and Wiegand, *J. prakt. Chem.*, 1932, **134**, 82.

m. p. 189°. This differed from 5 : 6-benzophenanthridine, m. p. 109—110°, synthesised by an unambiguous method (see below). The formation, from the dehydrogenation product, of a readily decomposed *scarlet* picrate eliminated any alternative benzophenanthridine type of structure and from its ultraviolet absorption spectrum (Fig. 1) the product was recognised as 1 : 2 : 8 : 9-dibenzacridine (IV), and proved identical with an authentic specimen.[5] The initial product of the reaction is presumably a di- or tetra-hydro-1 : 2 : 8 : 9-dibenzacridine. How such a structure is produced is not clear. With hot formic acid 2-α- and 2-β-naphthyliminomethyl-1-tetralone gave merely small yields of 1- and 2-formamidonaphthalene respectively.

Encouraged by the efficient cyclisation achieved [6] with 2-formamidodiphenyl we next considered the use of 1-*o*-acylaminophenylnaphthalenes as sources of 5 : 6-benzophenanthridines. The method was successful but suffers from the inaccessibility of 1-*o*-nitroarylnaphthalenes,[7] for the Ullmann reactions by which these were obtained gave very poor yields with increased scale. The derived amines [1-*o*-aminophenyl-, 1-(2-amino-4-methylphenyl)-, and 1-(2-amino-6-methylphenyl)-naphthalene [7]] were readily acetylated and formylated. Many cyclisation experiments were carried out with 1-*o*-acetamidophenylnaphthalene, the best yield (39%) of 9-methyl-5 : 6-benzophenanthridine (I; R′ = R″ = H, R = Me) being obtained by using a mixture of phosphorus oxychloride and stannic chloride. The appropriate acyl compounds provided 2 : 9- (I; R = R′ = Me, R″ = H) and 4 : 9-dimethyl-5 : 6-benzophenanthridine (I; R = R″ = Me, R′ = H).

In contrast to these cyclisations of acetamido-compounds (which gave yellow reaction solutions), those of formamido-compounds quickly led to very deep red solutions. However, by using short reaction times, moderate to poor yields of 5 : 6- (I; R = R′ = R″ = H), 2-methyl-5 : 6- (I; R = R″ = H, R′ = Me), and 4-methyl-5 : 6-benzophenanthridine (I; R = R′ = H, R″ = Me) were obtained.

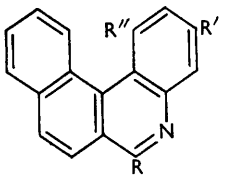
The difficulty of preparing 1-*o*-acylaminophenylnaphthalenes in quantity suggested the study of 1-amino-2-α-naphthyl*cyclo*hexane (V). 4-α-Naphthyl-5-nitro*cyclo*hexene was readily obtained from 1-2′-vinylnaphthalene [8] and butadiene, and reduced to 1-α-naphthyl-2-nitro*cyclo*hexane. With hydrogen and Raney nickel this gave the amine as a yellow oil which provided homogeneous acetyl and benzoyl derivatives. Analogy [9] suggests that the 1-2′-nitrovinylnaphthalene used in these experiments is the *trans*-isomer, and consequently the established stereochemical course of Diels–Alder reactions indicates *trans*-configurations for this 2-α-naphthyl*cyclo*hexylamine, its acetyl and benzoyl derivatives, and its precursors. As expected,[10] the *trans*-amine gave with phthalic anhydride the imide rather than the phthalamic acid. Reduction of *trans*-1-α-naphthyl-2-nitro*cyclo*hexane with lithium aluminium hydride, and subsequent acetylation, gave a mixture of isomers which could not be separated in practicable amounts. One isomer was identical with *trans*-1-acetamido-2-α-naphthyl*cyclo*hexane already mentioned, and the other was obviously the *cis*-isomer.[11]

Attempts to cyclise *trans*-1-acetamido- or *trans*-1-benzamido-2-α-naphthyl*cyclo*hexane with a number of reagents failed, and the azomethine formed from the amine and formaldehyde was merely hydrolysed under Pictet–Spengler conditions. These failures may be due to the *trans*-configuration of the amine, the known stereochemical oddness of α-naphthyl*cyclo*hexane derivatives,[12] or the insufficient activation of the naphthalene nucleus, although the successful cyclisation [13] of *N*-formyl-1-methyl-2-phenylpropylamine makes the last possibility unlikely.

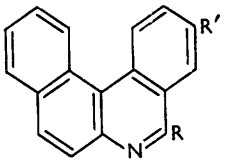
cis-2-α-Naphthyl*cyclo*hexylamine would probably be obtainable through 2-α-naphthyl-*cyclo*hexanone, but no practicable synthesis of this ketone has been reported.[14]

[5] Senier and Austin, *J.*, 1906, 1396.
[6] Ockenden and Schofield, *J.*, 1953, 717.
[7] Forrest and Tucker, *J.*, 1948, 1137; Tucker and Whalley, *J.*, 1949, 3213.
[8] Mayer and Sieglitz, *Ber.*, 1922, **55**, 1835.
[9] Goebel and Wenzke, *J. Amer. Chem. Soc.*, 1938, **60**, 697.
[10] Klyne, " Progress in Stereochemistry," Butterworths, London, 1954, p. 63.
[11] Wildman and Norton, *J. Amer. Chem. Soc.*, 1954, **76**, 152.
[12] Cook and Lawrence, *J.*, 1936, 1431; Klemm and Hodes, *J. Amer. Chem. Soc.*, 1951, **73**, 5181.
[13] Witkop, *J. Amer. Chem. Soc.*, 1948, **70**, 1424.
[14] Orchin, *ibid.*, 1948, **70**, 495; Huang, *J. Org. Chem.*, 1954, **19**, 1363.

4-α-Naphthyl-5-nitro*cyclo*hexene gave no ketonic product in the Nef reaction (other failures with unsaturated compounds have been reported [15]), but 1-α-naphthyl-2-nitro-*cyclo*hexane provided moderately good yields of 2-α-naphthyl*cyclo*hexanone. Unfortunately, equal success was not achieved on the large scale.



(I)



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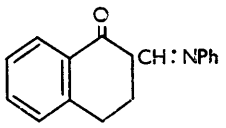

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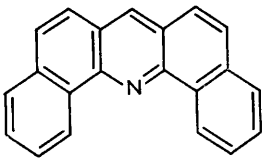

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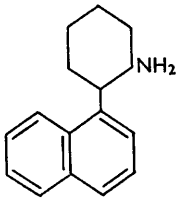

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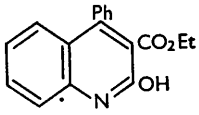

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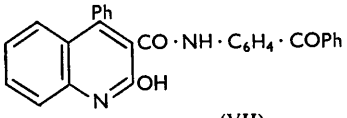


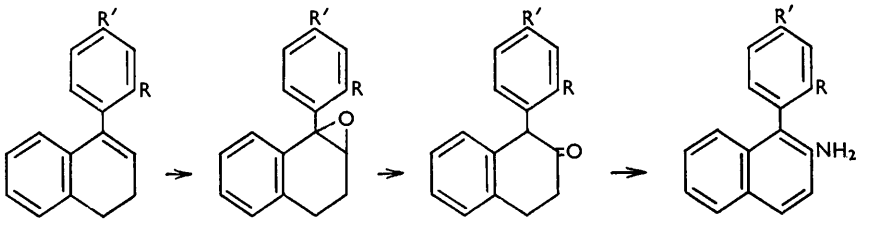
(VII)

One other approach to the 5 : 6-benzophenanthridine skeleton not yet successfully concluded deserves mention. We hoped to cyclise 4-phenyl-3-quinolylacetic acid. This might have been obtained from 4-phenylquinoline-3-carboxylic acid, prepared by Borsche and Sinn [16] in several stages from ethyl 2-hydroxy-4-phenylquinoline-3-carboxylate (VI). This ester was synthesised from ethyl malonate and *o*-aminobenzophenone, a later set of conditions [16b] being said to avoid formation of the anilide (VII) met in the earlier method.[16a] The original method gave us small yields of (VII) only, and the later conditions left the amine unchanged. By combining the two sets of conditions we obtained very good yields of the ester (VI) on several occasions, but, returning to the reaction later with different specimens of the reactants, inexplicably and despite repeated efforts we could isolate nothing but the amide (VII). This prevented us from completing the proposed synthesis, but with the available material we improved the preparation of 4-phenylquinoline-3-carboxylic acid. The acid chloride failed to undergo the Arndt–Eistert reaction, but by a malonic ester synthesis it provided 3-acetyl-4-phenylquinoline. In the Kindler–Willgerodt reaction this gave an unidentified product. 3-Acetyl-4-*o*-tolylquinoline was also prepared, but its use awaits clarification of the phenyl series. 3′-Oxoindeno(2′ : 1′-3 : 4)quinoline, obtained from 4-phenylquinoline-3-carboxylic acid, gave with diazomethane [17] 7(or 8)-methoxy-5 : 6-benzophenanthridine, isolated as its picrate. The yield did not encourage further examination of the reaction.

3 : 4-*Benzophenanthridines.*—Because of our success in cyclising 1-*o*-acylaminophenylnaphthalenes we examined the similar use of 2-acylamino-1-arylnaphthalenes. Zaugg, Freifelder, and Horrom [18] prepared 1-phenyl-2-naphthylamine (XI; R = R′ = H) from

[15] Tamelen and Thiede, *J. Amer. Chem. Soc.*, 1952, **74**, 2615.
[16] Borsche and Sinn, (*a*) *Annalen*, 1937, **532**, 146, (*b*) 1939, **538**, 283.
[17] Schutz, Schutz, and Cochran, *J. Amer. Chem. Soc.*, 1940, **62**, 2902; Badger, Carruthers, and Cook, *J.*, 1952, 4996.
[18] Zaugg, Freifelder, and Horrom, *J. Org. Chem.*, 1950, **15**, 1197.

3 : 4-dihydro-1-phenylnaphthalene by the processes (VIII—XI), and the ready availability of 1-aryl-3 : 4-dihydronaphthalenes made this an attractive route.



(VIII) (IX) (X) (XI)

Using the original conditions [18] in the 1-phenyl series we obtained a crude ketone which boiled over a very wide range. Variations in the amount of perbenzoic acid used in the initial step, and even omission of the sulphuric acid treatment which is supposed to isomerise the (oily) epoxide (IX ⟶ X), did not change the result significantly. In all cases distillation of the crude ketone gave two fractions with different (though not sharply separated) boiling ranges but giving comparable yields of oxime. The oxime melted over a wide range and may have been a mixture of isomers. Frequent and wasteful recrystallisation was required to produce a specimen with m. p. comparable to that reported by Zaugg *et al.*

With epoxidations in chloroform, the solvent used in the earlier work,[18] there is a tendency for aromatic rings to be attacked.[19] We therefore carried out the oxidation, (VIII; R = R' = H) ⟶ (IX; R = R' = H), in ether and thus obtained the epoxide in crystalline form and in good yield. With boron trifluoride–ether complex the solid epoxide gave a crude ketone which provided a good yield of oxime (again wide-melting), but which boiled over a wide range as before. Comparison of boron trifluoride and dilute sulphuric acid showed the former to be preferable for forming the ketone. A similar series of experiments were carried through with 3 : 4-dihydro-1-*p*-tolylnaphthalene. The oxime of 1-*p*-tolyl-2-tetralone so obtained was more nearly homogeneous than the phenyl compound and more easily purified.

3 : 4-Dihydro-1-*o*-tolylnaphthalene (VIII; R = Me, R' = H) (now obtained satisfactorily from α-tetralone and *o*-tolyl-lithium—the Grignard reagent gives unsatisfactory results [20]) was epoxidised considerably more slowly than the phenyl or the *p*-tolyl compound. The oily epoxide was converted into 1-*o*-tolyl-2-tetralone (X; R = Me, R' = H) but in no circumstances could more than a trace of the oxime be obtained from this ketone although the enol-acetate was prepared. The behaviour of the ketone recalls that of 4-*tert.*-butyl-3 : 4-dihydro-2-hydroxy-1-naphthyl mesityl ketone.[21]

With acetic anhydride, pyridine, and acetyl chloride,[22] 1-phenyl- and 1-*p*-tolyl-2-tetralone oxime gave good yields of 2-diacetylamino-1-phenyl- and -1-*p*-tolyl-naphthalene. The derived amines were easily monoacetylated and monoformylated. The small available quantity of 1-*o*-tolyl-2-tetralone oxime gave no recognisable product in attempts to aromatise it.

Phosphorus oxychloride–stannic chloride converted 2-acetamido-1-phenyl- and -1-*p*-tolyl-naphthalene into 9-methyl- (II; R = Me, R' = H) and 7 : 9-dimethyl-3 : 4-benzophenanthridine (II; R = R' = Me), respectively, in moderate yields. In this series the formamido-compounds behaved like the 1-*o*-formamidoarylnaphthalenes mentioned above, and from them only small yields of 7-methyl-3 : 4-benzophenanthridine (II; R = H, R' = Me) and 3 : 4-benzophenanthridine (II; R = R' = H) were isolable.

In this series also an attempt was made to extend the method of Hollingsworth and

[19] Gutsche and Fleming, *J. Amer. Chem. Soc.*, 1954, **76**, 1771.
[20] Friedel, Orchin, and Reggel, *ibid.*, 1948, **70**, 199; 1951, **73**, 1449.
[21] Fuson and Fang, *ibid.*, 1955, **77**, 3781.
[22] Beringer and Ugelow, *ibid.*, 1953, **75**, 2635.

Petrow,[3] but with hot formic acid the anil derived from β-naphthylamine and 2-hydroxymethylene-6-methyl*cyclo*hexanone gave only 2-formamidonaphthalene. Repetition of this method for preparing 5 : 6 : 7 : 8-tetrahydro-3 : 4-benzophenanthridine is described below.

FIG. 1. 1 : 2 : 8 : 9-*Dibenzacridine* (1); 3 : 4-*benzophenanthridine* (2).

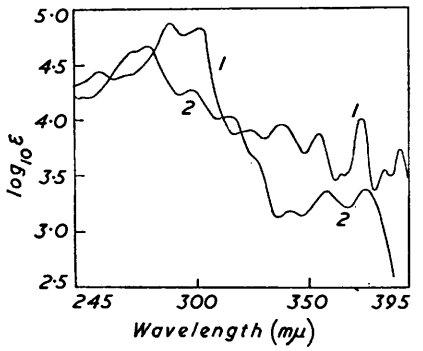
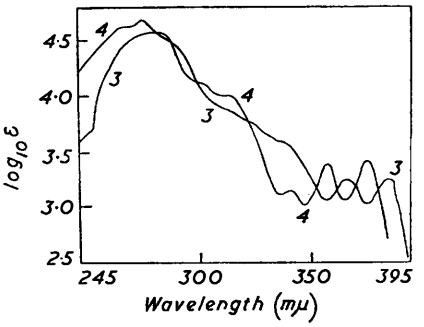


FIG. 2. 4-*Methyl-* (3). *and* 9-*methyl-*5 : 6-*benzophenanthridine* (4).



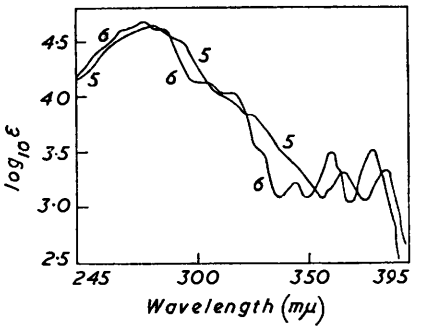


FIG. 3. 4 : 9-*Dimethyl-* (5), *and* 2 : 9-*dimethyl-*5 : 6-*benzophenanthridine* (6).

*Ultraviolet absorption spectra (in absolute ethanol).**

Compound	$\lambda_{max.}$ (mμ)								$\log_{10} \varepsilon_{max.}$							
5 : 6-Benzophenanthridine																
Unsubstd.	—	272	*283*	*308*	*315*	*326*	341	358	376	—	4·57	*4·44*	*3·9*	*3·83*	*3·43*	3·04	3·26	3·30
2-Methyl-	—	273	*284*	*305*	*317*	*328*	344	361	379	—	4·69	*4·61*	*4·03*	*3·96*	*3·56*	3·27	3·48	3·52
4-Methyl-	—	278	*291*	*313*	*339*	—	—	366	384	—	4·58	*4·43*	*3·87*	*3·57*	—	—	3·25	3·26
9-Methyl-	*266*	273	*284*	*301*	*316*	—	341	357	375	*4·61*	4·66	*4·55*	*4·12*	*3·98*	—	3·16	3·38	3·42
2 : 9-Dimethyl-	—	276	*286*	*302*	*316*	*328*	343	360	378	—	4·66	*4·59*	*4·13*	*4·02*	*3·51*	3·21	3·46	3·51
4 : 9-Dimethyl-	—	280	*296*	*316*	*325*	—	—	366	384	—	4·62	*4·42*	*3·95*	*3·81*	—	—	3·31	3·31
3 : 4-Benzophenanthridine																
Unsubtd.	*269*	278	297	314	*326*	341	358	375	—	*4·58*	4·65	4·27	4·02	*3·61*	3·16	3·36	3·37	—
9-Methyl-	*272*	278	298	314	*328*	*343*	356	374	—	*4·63*	4·66	4·34	4·11	*3·82*	*3·19*	3·41	3·45	—
7 : 9-Dimethyl-	—	276	296	314	328	343	356	374	—	—	4·62	4·24	4·06	3·65	3·18	3·43	3·47	—
1 : 2-8 : 9-Dibenz-acridine	256	288	302	324	337	354	364	374	—	4·44	4·86	4·82	3·90	3·95	3·86	3·50	4·0	
	384	391								3·54	3·73							
Di(?)hydro-1 : 2-8 : 9-dibenz-acridine	245	280	292	*302*	*326*	335				4·38	3·91	3·85	*3·58*	*4·09*	4·12			

* Figures in italics refer to shoulders or inflexions.

All of the 3 : 4- and 5 : 6-benzophenanthridines now synthesised exhibited characteristic blue fluorescence in solution. In the 3 : 4-benzophenanthrene series[2] the 5-methyl derivatives show m. p.s considerably higher than those of the other members, and in contrast do not form picrates. With the 5 : 6-benzophenanthridines the 4-methyl and the 4 : 9-dimethyl compound melt considerably higher than the parent and the other monomethyl derivatives, but so does 2 : 9-dimethyl-5 : 6-benzophenanthridine. All these

compounds formed stable picrates, which like those of the 3 : 4-benzophenanthridines were very insoluble. (It is obvious from the work of Petrow [23] and of Hollingsworth and Petrow [3] and from our own experiments that in the report by Kenner, Ritchie, and Wain [24] the m. p.s of benzophenanthridines and benzacridines became transposed.)

The ultraviolet extinction curve of 5 : 6-benzophenanthridine is almost identical with those of the 2- and 9-methyl, and 2 : 9-dimethyl derivatives (see Figures and Table). In contrast, the extinction curves of 4-methyl- and 4 : 9-dimethyl-5 : 6-benzophenanthridine, though generally similar to the others, show loss of detail with bathochromic, and for the long-wavelength peaks hypochromic shifts relative to the curves of their isomers. These changes parallel closely those observed in the 3 : 4-benzophenanthrene series [2] and indicate considerable intramolecular overcrowding in 4-methyl- and 4 : 9-dimethyl-5 : 6-benzophenanthridine.

Experimental

2-Phenyliminomethyl-1-tetralone.—2-Hydroxymethylene-1-tetralone [25] (0·2 g.), aniline (0·12 g.), and ethanol (1 c.c.) were heated on the steam-bath for ½ hr. The product (0·25 g.) which separated on cooling was digested with boiling light petroleum (b. p. 60—80°), leaving a yellow solid (0·1 g.; m. p. 105—112°) undissolved. Recrystallised from ethanol it gave m. p. 130—133°. Evaporation of the extract gave small orange plates (0·14 g.), m. p. 72—74°.

The same quantities of reagents left for 24 hr. at room temperature gave 0·01 g. of the orange substance and 0·19 g. of the yellow compound, or heated at 150° for ¼ hr. without ethanol, 0·15 g. of the former, and 0·06 g. of the latter. These *forms*, recrystallised from ethanol, formed orange needles, m. p. 72—75° (Found: C, 81·8; H, 6·1. $C_{17}H_{15}ON$ requires C, 81·9; H, 6·0%), and yellow needles, m. p. 131—133° (Found: C, 81·6; H, 6·5%), respectively ($\lambda_{max.}$ 262 and 400 mμ; $\log_{10}\varepsilon$ 4·23 and 4·45).

The lower-melting form of the anil (1 g.), ethanol (3 c.c.), hydroxylamine hydrochloride (1·4 g.), and water (2 c.c.) were set aside for 16 days. The solution was diluted with water and extracted with ether. The dried extract provided an *iso*oxazole,[26] b. p. 180—184°/14 mm. This (0·3 g.) in ether (5 c.c.) was added to a cold solution of sodium (0·2 g.) in methanol (2 c.c.). After 12 hr. the solution was concentrated, fine needles of 2-cyano-1-tetralone (0·17 g.), m. p. 72—75°, separating. The higher-melting form of the anil gave the same result.

2-Aryliminomethyl-1-tetralones.—The following were obtained by boiling equivalent quantities of 2-hydroxymethylene-1-tetralone and the amine in ethanol for 15 min., and recrystallising the products from ethanol: 2-p-*Tolyl-* (55%), orange needles, m. p. 144—145° (Found: C, 82·2; H, 6·1. $C_{18}H_{17}ON$ requires C, 82·1; H, 6·5%), 2-o-*tolyl-* (62%), yellow needles, m. p. 76—78° (Found: C, 82·1; H, 6·1%), 2-p-*methoxyphenyl-* (60%), yellow needles, m. p. 89—91° (Found: C, 77·3; H, 6·0. $C_{18}H_{17}O_2N$ requires C, 77·4; H, 6·1%), and 2-α-*naphthyl-iminomethyl-1-tetralone* (98%), yellow needles, m. p. 122—124° (Found: C, 83·9; H, 5·8. $C_{21}H_{17}ON$ requires C, 84·25; H, 5·7%).

Treatment of 2-Aryliminomethyl-1-tetralones with Formic Acid.—2-Phenyliminomethyl-1-tetralone (1 g.) and 96% formic acid (100 c.c.) were refluxed for 36 hr. The resulting red solution, which showed a strong green fluorescence, was concentrated at reduced pressure, and the residue was basified and extracted with ether. Evaporation of the dried (Na_2SO_4) extract and recrystallisation of the product from ethanol gave yellow crystals (0·4 g.). In subsequent experiments the yield was always much lower. In the same way the *o*-tolyl (0·47 g.), *p*-tolyl (0·5 g.), and *p*-methoxyphenyl analogues (0·5 g.) gave the same product (0·06, 0·09, and 0·04 g. respectively). *Tetra(?)hydro-1 : 2 : 8 : 9-dibenzacridine* formed yellow plates or needles, m. p. 159—160° (Found: C, 89·4; H, 6·3; N, 4·8. $C_{21}H_{17}N$ requires C, 89·0; H, 6·05; N, 4·9%), from ethanol.

This compound was heated with an equal weight of palladium–charcoal (30%) for 2 hr. under nitrogen at 250°. Sublimation and recrystallisation from acetone gave pale cream needles of 1 : 2 : 8 : 9-dibenzacridine, m. p. 189—190° (Found: C, 89·0; H, 4·7; N, 5·2. Calc. for $C_{21}H_{13}N$: C, 90·3; H, 4·7; N, 5·0%), which showed a strong, almost purple fluorescence

[23] Petrow, *J.*, 1942, 693.
[24] Kenner, Ritchie, and Wain, *J.*, 1937, 1526.
[25] Ott and Tarbell, *J. Amer. Chem. Soc.*, 1952, **74**, 6269.
[26] von Auwers and Rold, *J. prakt. Chem.*, 1937, **150**, 57; Johnson and Shelberg, *J. Amer. Chem. Soc.*, 1945, **67**, 1745.

in acetone and a pale blue fluorescence in concentrated sulphuric acid, and was identical (mixed m. p.) with an authentic specimen. The picrate, which easily dissociated, crystallised from a small volume of acetone as scarlet needles, m. p. 193—194°, alone and mixed with an authentic specimen.

1-o-*Acylaminophenylnaphthalenes.*—1-*o*-Aminophenylnaphthalene (1·46 g.) and formic acid (70 c.c.) were refluxed for 6 hr. Removal of the acid at reduced pressure, and crystallisation of the residue from benzene–light petroleum (b. p. 60—80°) gave needles of 1-o-*formamidophenylnaphthalene* (1·31 g.), m. p. 121—123° (Found : C, 82·3; H, 5·7. $C_{17}H_{13}ON$ requires C, 82·6; H, 5·3%). Similarly, 1-(2-amino-6-methylphenyl)- (0·6 g.) and 1-(2-amino-4-methylphenyl)-naphthalene (0·2 g.) gave, respectively, 1-(2-*formamido*-6-*methylphenyl*)- (0·52 g.), needles, m. p. 131—133° (Found : C, 82·0; H, 5·9. $C_{18}H_{15}ON$ requires C, 82·7; H, 5·8%), and 1-(2-*formamido*-4-*methylphenyl*)-*naphthalene* (0·2 g.), needles, m. p. 155—157° (Found : C, 82·7; H, 5·8%).

1-*o*-Aminophenylnaphthalene (0·49 g.), acetic anhydride (0·5 g.), and dry benzene (5 c.c.) were refluxed for 4 hr. Concentration at reduced pressure and crystallisation of the residue from ethyl acetate–light petroleum (b. p. 60—80°) gave needles (0·16 g.) of 1-o-*acetamidophenylnaphthalene*, m. p. 95—96° (Found : C, 81·8; H, 5·8. $C_{18}H_{15}ON$ requires C, 82·7; H, 5·8%). Similarly, the appropriate amines (0·26 and 0·2 g. respectively) gave 1-(2-*acetamido*-6-*methylphenyl*)- (0·25 g.), m. p. 104—105° (Found : C, 82·8; H, 6·2. $C_{19}H_{17}ON$ requires C, 82·9; H, 6·2%), and 1-(2-*acetamido*-4-*methylphenyl*)-*naphthalene*, needles (0·21 g.), m. p. 127—128° (Found : C, 82·85; H, 6·2%), from benzene.

5 : 6-*Benzophenanthridines.*—The following conditions, the most satisfactory of many used, illustrate the general method. 1-*o*-Acetamidophenylnaphthalene (0·64 g.), phosphorus oxychloride (20 c.c.), and anhydrous stannic chloride (0·96 g.) were refluxed for 8 hr. Most of the phosphorus oxychloride was then removed at reduced pressure and the chilled residue was treated with water and aqueous ammonia. Extraction with benzene gave a product which from benzene–light petroleum formed pale yellow prisms (0·23 g.) of 9-*methyl*-5 : 6-*benzophenanthridine*, m. p. 93—94° (Found : C, 88·7; H, 4·9; N, 5·7. $C_{18}H_{13}N$ requires C, 88·9; H, 5·35; N, 5·8%). Prepared in alcohol, and recrystallised from 2-ethoxyethanol, the *picrate* formed yellow needles, m. p. 210—215° (decomp.) (Found : C, 61·2; H, 3·5; N, 12·5. $C_{18}H_{13}N,C_6H_3O_7N_3$ requires C, 61·0; H, 3·4; N, 11·9%).

The conditions used in other cases are tabulated.

1-Arylnaphthalene	Wt. (g.)	$POCl_3$ (c.c.)	$SnCl_4$ (g.)	Time	Yield (g.)	Product
o-Formamidophenyl	0·5	10	1·06	4 hr.	0·08	*a*
2-Formamido-4-methylphenyl	0·1	5	0·2	10 min.	0·02	*b*
2-Formamido-6-methylphenyl	0·2	5	0·4	3 hr.	0·06	*c*
2-Acetamido-4-methylphenyl	0·55	30	1·07	5 hr.	0·14	*d*
2-Acetamido-6-methylphenyl	0·2	8	0·28	8 hr.	0·06	*e*

The picrates of the products were all prepared in alcohol and recrystallised from 2-ethoxyethanol. The products were :

(*a*) 5 : 6-*Benzophenanthridine*, needles, m. p. 109—110° (Found : C, 89·1; H, 5·0. $C_{17}H_{11}N$ requires C, 88·45; H, 5·1%), from acetone. *Picrate*, yellow needles, m. p. 253—255° (Found : C, 60·0; H, 3·0; N, 13·4. $C_{17}H_{11}N,C_6H_3O_7N_3$ requires C, 60·3; H, 2·8; N, 12·2%).

(*b*) 2-*Methyl*-5 : 6-*benzophenanthridine*, prisms, m. p. 115—116° (Found : C, 88·9; H, 5·45. $C_{18}H_{13}N$ requires C, 88·9; H, 5·4%), from benzene–light petroleum (b. p. 60—80°).

(*c*) 4-*Methyl*-5 : 6-*benzophenanthridine*, prisms, m. p. 180—182° (Found : C, 87·4; H 5·6%), from acetone. *Picrate*, yellow needles, m. p. 220° (Found : C, 61·6; H, 3·4. $C_{18}H_{13}N,C_6H_3O_7N_3$ requires C, 61·0; H, 3·4%).

(*d*) 2 : 9-*Dimethyl*-5 : 6-*benzophenanthridine*, yellow needles, m. p. 171—172° (Found : C, 88·0; H, 5·7. $C_{19}H_{15}N$ requires C, 88·7; H, 5·9%), from benzene–light petroleum (b. p. 60—80°). *Picrate*, yellow needles, m. p. 264° (Found : C, 61·8; H, 3·9; N, 11·7. $C_{19}H_{15}N,C_6H_3O_7N_3$ requires C, 61·7; H, 3·7; N, 11·5%).

(*e*) 4 : 9-*Dimethyl*-5 : 6-*benzophenanthridine*, yellow needles, m. p. 150—151° (Found : C, 88·7; H, 4·9%), from ether–light petroleum (b. p. 60—80°). *Picrate*, yellow needles, m. p. 230° (Found : C, 61·9; H, 3·8%).

4-α-*Naphthyl*-5-*nitrocyclohexene.*—1-2′-Nitrovinylnaphthalene (7·5 g.), butadiene (6·1 g.), toluene (10 c.c.), and a trace of quinol were heated in a sealed tube (evacuated to 30 mm. pressure) for 2 days at 100°. The cold tube was opened and excess of butadiene was removed by gentle heating, the toluene was evaporated, and the residue was recrystallised

from ethanol, giving pale yellow needles of 4-α-*naphthyl*-5-*nitro*cyclo*hexene* (4·9 g.), m. p. 124—125° (Found: C, 76·0; H, 6·0; N, 5·3. $C_{16}H_{15}O_2N$ requires C, 75·9; H, 6·0; N, 5·5%). The yield varied from 52% to 62%.

trans-1-α-*Naphthyl*-2-*nitro*cyclo*hexane*,—The above compound (9·8 g.), acetic acid (300 c.c.), and platinum oxide (0·4 g.) were shaken with hydrogen. Reduction was complete in 2½ hr., then the mixture was filtered and concentrated. From methanol the residual oil gave needles (8·7 g.) of trans-1-α-*naphthyl*-2-*nitro*cyclo*hexane*, m. p. 96—98° (Found: C, 74·7; H, 6·8; N, 5·4. $C_{16}H_{17}O_2N$ requires C, 75·3; H, 6·7; N, 5·5%).

trans-2-α-*Naphthyl*cyclo*hexylamine*.—The nitro-compound (4 g.) in ethanol was reduced with hydrogen in the presence of Raney nickel (20 c.c. of settled suspension). Reduction was complete in 5 hr., and, in the usual way, the amine (2·3 g.) was isolated as a pale yellow viscous oil, b. p. 160—164°/0·05 mm.

The amine (0·2 g.), acetic anhydride (0·14 g.), and dry pyridine were heated at 100° for 3 hr. The solution was poured into water, and the product (0·19 g.) crystallised from benzene, giving small needles of trans-1-*acetamido*-2-α-*naphthyl*cyclo*hexane*, m. p. 178—179° (Found: C, 80·6; H, 7·7. $C_{18}H_{21}ON$ requires C, 80·9; H, 7·9%).

In the same way the amine (0·2 g.), benzoyl chloride (0·14 g.), and pyridine (5 c.c.) gave the *benzamido-compound* (0·25 g.) which separated from ethanol as needles, m. p. 192—193° (Found: C, 83·5; H, 7·2. $C_{22}H_{23}ON$ requires C, 83·2; H, 7·3%).

When the amine (0·2 g.) and phthalic anhydride (0·13 g.) were refluxed for 7 hr. in chlorobenzene (5 c.c.) removal of the solvent at reduced pressure gave an oil which solidified on trituration with benzene–light petroleum (b. p. 60—80°). Crystallisation from acetone gave prisms (0·12 g.) of trans-2-α-*naphthyl*-1-*phthalimido*cyclo*hexane*, m. p. 192—194° (Found: C, 80·9; H, 5·9. $C_{24}H_{21}O_2N$ requires C, 81·1; H, 6·0%).

Lithium Aluminium Hydride Reduction of trans-1-α-*Naphthyl*-2-*nitro*cyclo*hexane*.—The nitro-compound (3 g.) in ether (90 c.c.) was added dropwise to a gently refluxing solution of lithium aluminium hydride (1·4 g.) in ether (100 c.c.). After refluxing for 4 hr. the mixture was treated with water and dilute aqueous sodium hydroxide. Thorough extraction with ether and evaporation of the dried (Na_2SO_4) extract gave an oil (2·1 g.) which was heated for 3 hr. at 100° with acetic anhydride (1·43 g.) and pyridine (30 c.c.). The acetylation solution was decomposed with water and extracted with ether. Drying (Na_2SO_4), evaporation, and removal *in vacuo* of the last traces of pyridine gave an oil from which, on addition of ether, a solid (1·62 g.), m. p. 144—146°, separated. (Concentration of the ethereal layer gave 0·24 g. of an oil, probably unchanged amine.) The solid was crystallised three times from benzene, and the more soluble fractions were combined and passed in benzene over alumina. The first two fractions (0·13 g.), m. p. 181—183°, gave no m. p. depression when mixed with the acetyl derivative prepared from the Raney nickel reduction product. The last two fractions (0·05 g.) were recrystallised from benzene, giving needles of the cis-*acetamido-compound*, m. p. 182—185° (Found: C, 80·6; H, 7·9%), which gave a strong m. p. depression when mixed with the *trans*-compound.

2-α-*Naphthyl*cyclo*hexanone*.—1-α-Naphthyl-2-nitro*cyclo*hexane (0·5 g.) in absolute ethanol (20 c.c.) was treated with a solution of sodium (0·1 g.) in ethanol (5 c.c.) and set aside for 1 hr. under nitrogen. The pale green solution was added dropwise to concentrated hydrochloric acid (8 c.c.), water (30 c.c.), and ethanol (25 c.c.) under nitrogen at 0° and stirred for 1½ hr. at this temperature. After being stirred for 8 hr. at room temperature the yellow solution was diluted with water and extracted with ether. Evaporation of the dried (Na_2SO_4) extract gave an oil (0·4 g.) which was heated for 10 min. on the steam-bath with semicarbazide hydrochloride (0·5 g.), and sodium acetate (1 g.) in water with sufficient ethanol to ensure homogeneity. Chilling the solution gave 2-α-naphthyl*cyclo*hexanone semicarbazone (0·34 g., 64%), m. p. 208—210° (Found: C, 72·5; H, 6·8; N, 13·6. Calc. for $C_{17}H_{19}ON_3$: C, 72·6; H, 6·8; N, 14·9%), which formed fawn needles from ethanol. Orchin [14] gave m. p. 213—215°. This yield could not be attained in larger-scale experiments.

Ethyl 2-*Hydroxy*-4-*phenylquinoline*-3-*carboxylate*.—*o*-Aminobenzophenone (15 g.) and ethyl malonate (30 g.) were heated together at 175—180° for 2 hr. Recrystallised from ethanol the product gave prisms (62%) of ethyl 2-hydroxy-4-phenylquinoline-3-carboxylate, m. p. 196—198°. Experiments on one-third of this scale gave 89% of the ester.

Ethyl 2-*Hydroxy*-4-o-*tolylquinoline*-3-*carboxylate*.—2-Amino-2′-methylbenzophenone (0·44 g.) and ethyl malonate were heated for 1 hr. at 175—180°. Crystallisation from ethanol gave prisms (0·41 g.) of *ethyl* 2-*hydroxy*-4-o-*tolylquinoline*-3-*carboxylate*, m. p. 171—173° (Found: C, 74·2: H, 5·7. $C_{19}H_{17}O_3N$ requires C, 74·3; H, 5·6%).

Ethyl 2-*Chloro*-4-*phenylquinoline*-3-*carboxylate*.—The hydroxy-compound (3·75 g.) and phosphorus oxychloride (11·3 c.c.) were refluxed for 1 hr. The solution was concentrated under reduced pressure and the residue was decomposed with ice and aqueous sodium hydroxide and extracted with ether. Evaporation of the dried (Na_2SO_4) extract gave the *chloro-compound* (3·05 g.), which formed yellow needles, m. p. 104—106° (Found: C, 69·6; H, 4·6; N, 4·3. $C_{18}H_{14}O_2NCl$ requires C, 69·3; H, 4·5; N, 4·5%), from ethanol.

Ethyl 2-*Chloro*-4-o-*tolylquinoline*-3-*carboxylate*.—In the same way the hydroxy-*o*-tolyl compound (2·3 g.) gave the *chloro-compound* (1·4 g.), which formed plates, m. p. 121—123° (Found: C, 70·4; H, 5·0. $C_{19}H_{16}O_2NCl$ requires C, 70·0; H, 5·0%), from ethanol.

4-*Phenylquinoline*-3-*carboxylic Acid*.—Ethyl 2-chloro-4-phenylquinoline-3-carboxylate (3 g.), red phosphorus (1·5 g.), and hydriodic acid (12 c.c.; *d* 1·7) were refluxed together for 8 hr. Most of the hydriodic acid was then removed, and the residue was thoroughly extracted with boiling aqueous sodium carbonate. The extract was just acidified (Congo-red) with hydrochloric acid, boiled, and filtered hot. The cooled filtrate was treated with sodium acetate, and the product was crystallised from acetic acid. It formed needles (2·15 g.), m. p. 228—230°.

4-o-*Tolylquinoline*-3-*carboxylic Acid*.—The chloro-compound (1·2 g.), hydriodic acid (9·6 c.c.), and red phosphorus (0·6 g.) were refluxed for 7 hr. The mixture was worked up as before and the product was precipitated by bringing the alkaline extract to pH 5—6 with hydrochloric acid. The *acid* (0·77 g.) formed needles, m. p. 235—236° (Found: C, 74·0; H, 5·2. $C_{17}H_{13}O_2N,H_2O$ requires C, 75·0; H, 5·2%), from acetic acid.

3-*Acetyl*-4-*phenylquinoline*.—The acid chloride prepared from 4-phenylquinoline-3-carboxylic acid (2·5 g.) and thionyl chloride was suspended in dry benzene (40 c.c.) and added rapidly to ethyl sodiomalonate (from 4·75 g. of the ester) in benzene (100 c.c.). The mixture was refluxed for ½ hr., treated with water, and extracted with benzene. Evaporation of the extract gave a small amount of an oil. Neutralisation of the aqueous layer gave the ether-soluble product, which on crystallisation from ethanol provided pale yellow needles (1·3 g.) of *ethyl* 4-*phenyl*-3-*quinolylcarbonylmalonate*, m. p. 106—107° (Found: C, 70·9; H, 5·4. $C_{23}H_{21}O_5N$ requires C, 70·6; H, 5·4%). A similar experiment with 4 g. of the acid gave 3·3 g. of product.

When the quinoline acid (0·5 g.) was treated as above but the solution obtained on decomposition with water was left overnight before being worked up, long, crisp needles (0·33 g.) of a *product*, m. p. 193—200° (decomp.) (Found: C, 63·5; H, 5·2. $C_{21}H_{17}O_5N,2H_2O$ requires C, 63·2; H, 5·3%), separated from the aqueous layer. It was probably a dihydrate of the half ester of 4-phenyl-3-quinolylcarbonylmalonic acid.

Ethyl 4-phenyl-3-quinolylcarbonylmalonate (2·21 g.) and 20% sulphuric acid (100 c.c.) were refluxed together for 3 hr. The cooled solution was basified and extracted with ether. The dried (Na_2SO_4) extract gave on evaporation 3-*acetyl*-4-*phenylquinoline* which separated as yellow needles (1·15 g.), m. p. 76—78° (Found: C, 82·7; H, 5·2. $C_{17}H_{13}ON$ requires C, 82·6; H, 5·3%), from light petroleum (b. p. 60—80°).

When this ketone (1·15 g.), sulphur (0·46 g.), and morpholine (6 c.c.) were refluxed for 13 hr. and the solution was poured into ethanol, an orange solid separated. This *substance* formed orange needles (0·8 g.), m. p. 202—204° (Found: C, 65·0; H, 5·6; N, 8·3%), from ethanol. Attempts to hydrolyse the product with mixtures of acetic acid and sulphuric acid were unsuccessful.

3-*Acetyl*-4-o-*tolylquinoline*.—To ethyl sodiomalonate (from 0·37 g. of the ester) in benzene (15 c.c.), 4-*o*-tolylquinoline-3-carboxylic acid chloride (from 0·2 g. of the acid) in benzene (15 c.c.) suspension was added rapidly, and the mixture was refluxed for 1 hr. Water was added and the aqueous layer was separated. Neutralisation gave no organic material. The benzene layer was concentrated and shaken with dilute hydrochloric acid. Ether was added, and the organic layer was separated, dried (Na_2SO_4), and evaporated, leaving a reddish oil (0·17 g.) which could not be crystallised. This oil (0·59 g.) and 20% sulphuric acid (30 c.c.) were refluxed for 4 hr. The yellow solution was decanted from some black oil, cooled, basified, and extracted with ether. The dried (Na_2SO_4) extract provided an oil (0·34 g.) which from light petroleum (b. p. 40—60°) gave yellow prisms of 3-*acetyl*-4-o-*tolylquinoline*, m. p. 92—94° (Found: C, 82·7; H, 5·4; N, 5·3. $C_{18}H_{15}ON$ requires C, 82·7; H, 5·8; N, 5·4%).

7(or 8)-*Methoxy*-5 : 6-*benzophenanthridine*.—3′-Oxoindeno(2′ : 1′-3 : 4)quinoline [1] (0·31 g.) and ethereal diazomethane (*ca.* 20 equivs.) were set aside for 16 hr. at 5°. After 36 hr. more at room temperature the solution was concentrated at reduced pressure, giving a brown gum (0·27 g.). Passage in benzene over alumina gave a sticky solid which darkened in air and showed blue fluorescence in benzene. With picric acid in ethanol it gave 7(or 8)-*methoxy*-5 : 6-*benzophenanthridine picrate* which separated as a bright yellow powder (0·1 g.), m.p. 224—232°

(decomp.) (Found: C, 59·1; H, 3·5. $C_{18}H_{13}ON,C_6H_3O_7N_3$ requires C, 59·0; H, 3·3%), from 2-ethoxyethanol.

1-*Phenyl*-2-*tetralone*.—(*a*) Perbenzoic acid (8·3 g.) in ether (135 c.c.) was added with stirring to 3 : 4-dihydro-1-phenylnaphthalene (11·25 g.) in ether (100 c.c.) at such a rate that the temperature did not rise above −2°. After being stirred for 9 hr. at 0° (preliminary titrations showed that the consumption of perbenzoic acid was almost complete in this time) the solution was washed with dilute aqueous sodium hydroxide and with water and then dried (Na_2SO_4). 3 : 4-*Dihydro*-1-*phenylnaphthalene epoxide* (7·5 g.) formed needles, m. p. 100—102° (Found: C, 86·9; H, 6·2. $C_{16}H_{14}O$ requires C, 86·5; H, 6·4%), from benzene–light petroleum (b. p. 60—80°).

The epoxide (3·2 g.) in dry ether (30 c.c.) was treated with boron trifluoride–ether complex (2·54 g.). After the initial exothermic reaction the brown solution was set aside for 17 hr. before being washed with dilute aqueous sodium hydroxide and water. The dried (Na_2SO_4) extract gave on evaporation and distillation a yellow oil (1·44 g.), b. p. 156—164°/2 mm., and a dark yellow oil (0·53 g.), b. p. 174—210°/2 mm. These fractions gave the oxime (see below) in comparable yields.

(*b*) A chloroform solution of the peracid was added slowly to 3 : 4-dihydro-1-phenylnaphthalene in chloroform, below −4°. The solution was then stirred at 0° for 2½ hr., washed with dilute aqueous sodium hydroxide and water, and dried (Na_2SO_4). After removal of the chloroform the oil was either distilled at once, or boiled with 30% sulphuric acid before being distilled. Some results are tabulated.

	Dihydro-cpd. in $CHCl_3$		Peracid in $CHCl_3$		Acid	Product	
Expt.	(g.)	(c.c.)	(g.)	(c.c.)	treatment	g.	b. p.
A	2·8	25	2·08	40	None	1·05	146—150°/0·5 mm.
						0·49	180—190°/ ,,
B	,,	,,	,,	,,	Given	1·12	150—154°/0·6 mm.
						0·62	160—184°/ ,,
C	2·26	30	2·28	44	None	1·01	150—154°/0·5 mm.
						0·69	174—210°/ ,,
D	13·07	100	9·6	105	None	4·45	140—146°/0·1 mm.
						2·77	156—178°/ ,,

A portion of the lower-boiling oil from expt. D which had been set aside for a long time at a temperature of *ca.* 10° gave crystals of the somewhat impure ketone, m. p. 39—41° (Found: C, 85·3; H, 6·1. Calc. for $C_{16}H_{14}O$: C, 86·5; H, 6·4%).

1-*Phenyl*-2-*tetralone Oxime*.—In all cases the ketone and 10 equivs. of hydroxylamine hydrochloride were refluxed in ethanol containing enough sodium hydroxide to make the solution alkaline. Usually the oxime separated in 10 min. The mixture was cooled in ice and the product was collected.

(*a*) From the ketone prepared from crystalline epoxide: The ketone (0·16 g.), b. p. 156—164°/2 mm., gave the oxime (0·12 g.), m. p. 162—174°. The crude ketone (2·65 g.) obtained directly from boron trifluoride rearrangement of the epoxide gave the oxime (2·1 g.), m. p. 162—173°.

(*b*) From the ketone prepared from the product of epoxidation in chloroform: In each experiment 1 g. of the oils obtained in the experiments described above was converted into oxime, which melted in the range 160—170° (see Table). The lower-boiling oil from expt. D

	Yield of oxime (g.)	
Expt.	From lower-boiling oil	From higher-boiling oil
A	0·75	1·0
B	—	0·95
C	0·75	0·68
D	0·54	0·56

(3·77 g.) gave the oxime (3·1 g.), m. p. 162—174°. Several crystallisations from ethanol gave plates, m. p. 178—180° (Found: C, 80·9; H, 6·4. Calc. for $C_{16}H_{15}ON$: C, 80·3; H, 6·4%).

1-p-*Tolyl*-2-*tetralone*.—(*a*) Perbenzoic acid (4·56 g.) in ether (110 c.c.) was added to a stirred solution of 3 : 4-dihydro-1-*p*-tolylnaphthalene (6·57 g.) in ether (100 c.c.) at −5°. Stirring was continued for 9 hr. at 0°. In the usual way the epoxide (7·2 g.) was isolated as a pale yellow oil. Distillation caused much decomposition but by this means a somewhat impure specimen, b. p. 146—148°/1 mm. (Found: C, 87·5; H, 7·0. Calc. for $C_{17}H_{16}O$: C, 86·4; H, 6·8%), was obtained. It did not react with hydroxylamine. In another experiment the ethylene (11·3 g.) gave 12·1 g. of crude epoxide.

The epoxide (11·8 g.) in ether (25 c.c.) was treated with boron trifluoride–ether complex (7·08 g.) at room temperature. After the initial reaction the solution was set aside for 18 hr. at room temperature, washed with dilute alkali and water, and dried (Na_2SO_4). Evaporation and distillation gave a yellow oil (2·93 g.), b. p. 185—195°/0·6 mm.

A similar experiment with 1 g. of epoxide in boiling benzene gave 0·94 g. of crude ketone.

(*b*) 3 : 4-Dihydro-1-*p*-tolylnaphthalene (9·4 g.) in chloroform (75 c.c.) was treated at −6° with perbenzoic acid (6·25 g.) in chloroform (134 c.c.). After being stirred for 3 hr. at 0° the solution was worked up as before to give (i) a solid (0·42 g.), b. p. 150—158°/10 mm., which furnished needles, m. p. 120—120·5° (Found: C, 65·5; H, 7·6%), from ethanol, (ii) a pale yellow oil (4·5 g.), b. p. 150—156°/0·4 mm., and (iii) a yellow viscous oil (1·36 g.), b. p. 172—178°/0·4 mm. The last two fractions both gave the oxime.

1-p-*Tolyl-2-tetralone Oxime.*—(*a*) The lower-boiling oil (2·7 g.) from the boron trifluoride rearrangement gave the crude oxime (2·2 g.), m. p. 164—168°. Recrystallisation from ethanol gave needles (0·92 g.), m. p. 169—171°, and the pure *oxime* showed m. p. 170—172° (Found: C, 81·2; H, 6·8. $C_{17}H_{17}ON$ requires C, 80·7; H, 6·9%). The higher-boiling oil (2·93 g.) gave 2·83 g. of crude material, and after crystallisation 1·38 g., m. p. 170—172°.

(*b*) The undistilled oil (0·9 g.) from an oxidation in chloroform gave 0·34 g. of crude oxime. In another experiment the oil (4·5 g.) gave finally 2·49 g. of pure oxime, m. p. 170—172°.

3 : 4-*Dihydro*-1-o-*tolylnaphthalene.*—α-Tetralone (20 g.) in ether (100 c.c.) was added slowly to a stirred solution of *o*-tolyl-lithium (from 70 g. of *o*-bromotoluene and 5·7 g. of lithium) in ether (300 c.c.). After being refluxed gently for 16 hr. the mixture was decomposed with ice and dilute hydrochloric acid, the ether layer was separated, and the aqueous layer was thoroughly extracted with ether. Evaporation of the combined, dried (Na_2SO_4) extracts and refluxing of the residual oil with concentrated hydrochloric acid (3 c.c.) in benzene (100 c.c.) gave a product which on distillation provided the dihydro-compound as a pale yellow oil (16·1 g.), b. p. 119—120°/0·2 mm. (Found: C, 93·5; H, 7·2. Calc. for $C_{17}H_{16}$: C, 92·7; H, 7·3%). This crystallised, and from light petroleum (b. p. 60—80°) gave massive, crisp rhombs, m. p. 53—55°. Heated with 30% palladium–charcoal at 150—160° for 2 hr., it gave 1-*o*-tolylnaphthalene, needles (from methanol), m. p. 61—63°. This compound strongly depressed the m. p. of the dihydro-compound when mixed with it.

1-o-*Tolyl-2-tetralone.*—To a solution of 3 : 4-dihydro-1-*o*-tolylnaphthalene (7·43 g.) in ether (50 c.c.), perbenzoic acid (5·13 g.) in ether (84 c.c.) was added with stirring, at −3° to −5°. After being stirred for 10 hr. at this temperature the solution was kept at 5° for 13 hr. and at room temperature for 3½ hr. (In parallel experiments it was found that at 0° 3 : 4-dihydro-1-phenylnaphthalene consumed 80% of the theoretical amount of perbenzoic acid in 8½ hr., whilst the *o*-tolyl compound required 22 hr. to reach this figure.) The crude epoxide (7·1 g.) was isolated as a clear yellow oil. This oil (6·74 g.) in anhydrous benzene (30 c.c.) was warmed on the steam-bath and boron trifluoride–ether complex (4·05 g.) in benzene (10 c.c.) was added cautiously. After 10 min. the benzene solution was washed with aqueous sodium hydroxide and with water, dried (Na_2SO_4), and evaporated, giving a viscous yellow oil (3·29 g.), b. p. 246—252°/0·8 mm. Redistillation gave 1-o-*tolyl-2-tetralone* (2·1 g.) as a sweet-smelling, yellow oil, b. p. 149—151°/0·4 mm. (Found: C, 85·8; H, 6·9. $C_{17}H_{16}O$ requires C, 86·4; H, 6·8%).

The ketone (0·42 g.), hydroxylamine hydrochloride (1·18 g.), 2N-sodium hydroxide (9 c.c.), and ethanol (6 c.c.) were refluxed for ½ hr. The chilled solution was extracted with ether. The oil obtained from the dried extract was dissolved in the minimum volume of ethanol; on cooling, the *oxime* (0·06 g.) separated as plates, m. p. 145—147° (Found: C, 80·7; H, 6·8%).

The ketone (0·5 g.), anhydrous sodium acetate (1 g.), and acetic anhydride (5 c.c.) were heated on the steam-bath for 62 hr. The solution was poured into water and the precipitated oil was extracted with ether. Drying (Na_2SO_4) and evaporation gave an oil which from light petroleum (b. p. 60—80°) provided needles of the *enol acetate* (0·1 g.), m. p. 97—99° (Found: C, 82·1; H, 6·6. $C_{19}H_{18}O_2$ requires C, 82·0; H, 6·5%).

1-*Phenyl-2-naphthylamine.*—1-Phenyl-2-tetralone oxime and 1 equiv. of pyridine in a large excess of acetic anhydride were kept in the refrigerator for 24 hr. Acetyl chloride (1 equiv.) was added and the solution was heated at 100° for 1 hr. Most of the solvent was removed at reduced pressure and water was added. The oil was dried (Na_2SO_4) in ether and crystallised from ethanol, to give needles of 2-diacetamido-1-phenylnaphthalene, m. p. 107—108° (Found: C, 78·4; H, 5·5. Calc. for $C_{20}H_{17}O_2N$: C, 79·2; H, 5·6%). From uncrystallised oxime (0·5, 0·27, 0·27 g.) the yields were 27, 21, and 22%. With once crystallised oxime (0·42, 0·31, 1·96 g.) yields were 65, 50, and 60%.

Hydrolysis of the diacetyl compound (1·8 g.) with boiling 1 : 1 aqueous hydrochloric acid

(10 c.c.) for 3½ hr. gave a crystalline hydrochloride. The base was liberated with ammonia, extracted with ether, and crystallised from light petroleum (b. p. 40—60°), giving fawn needles (0·83 g.) of 1-phenyl-2-naphthylamine, m. p. 93—94°. Heated with excess of anhydrous formic acid for 1 hr. at 100° this gave 2-*formamido*-1-*phenylnaphthalene* which formed prisms (70%), m. p. 121—123° (Found : C, 83·0; H, 5·7. $C_{17}H_{13}ON$ requires C, 82·6; H, 5·3%), from ethanol. Refluxing the amine with acetic anhydride (1·3 mols.) in benzene for 3 hr. gave 2-*acetamido*-1-*phenylnaphthalene* (100%) which formed rosettes of needles, m. p. 132—134° (Found : C, 82·5; H, 5·7. $C_{18}H_{15}ON$ requires C, 82·7; H, 5·8%), from benzene–light petroleum (b. p. 60—80°).

1-p-*Tolyl*-2-*naphthylamine*.—By the above method the appropriate pure oxime (1·38, 1·38, 0·8 g.) gave 2-*diacetamido*-1-p-*tolylnaphthalene* (65, 70, and 66%) which separated from ethanol as plates, m. p. 123—124° (Found : C, 79·4; H, 6·0. $C_{21}H_{19}O_2N$ requires C, 79·5; H, 6·0%). Hydrolysis as before gave 1-p-*tolyl*-2-*naphthylamine* (74%) which formed needles, m. p. 134—136° (Found : C, 87·4; H, 6·5. $C_{17}H_{15}N$ requires C, 87·5; H, 6·5%), from light petroleum (b. p. 60—80°). 2-*Formamido*-1-p-*tolylnaphthalene* separated from ethanol as prisms (83%), m. p. 160—162° (Found : C, 82·6; H, 6·1. $C_{18}H_{15}ON$ requires C, 82·7; H, 5·8%), and 2-*acetamido*-1-p-*tolylnaphthalene* from aqueous ethanol as prisms (83%), m. p. 125—126° (Found : C, 82·7; H, 6·2. $C_{19}H_{17}ON$ requires C, 82·9; H, 6·2%).

3 : 4-*Benzophenanthridine*.—(*a*) 2-Formamido-1-phenylnaphthalene (0·1 g.), phosphorus oxychloride (5 c.c.), and stannic chloride (0·16 g.) were refluxed for 1 hr. Excess of phosphorus oxychloride was removed at reduced pressure, and the dark red residue was basified and extracted with chloroform. The oil obtained from the chloroform gave, with picric acid in ethanol, 3 : 4-benzophenanthridine picrate which separated as a yellow powder, m. p. 229—233° (decomp.) (Found : C, 59·7; H, 3·1. Calc. for $C_{17}H_{11}N,C_6H_3O_7N_3$: C, 60·2; H, 3·1%), from 2-ethoxyethanol.

(*b*) 2-β-Naphthyliminomethyl*cyclo*hexanone (10 g.) was refluxed with formic acid (100 c.c.) for 20 hr. and worked up as usual. The resulting oil was treated with picric acid in ethanol, and the picrate was digested with hot ethanol, giving a brown powder (6·9 g.), m. p. 243—247°. The free base, liberated by lithium hydroxide, separated from light petroleum (b. p. 60—80°) as pale brown needles (2·82 g.), m. p. 92—95°. This (0·8 g.) and 30% palladium–charcoal (0·4 g.) were heated at 310—320° for 6 hr. under nitrogen. Crystallisation from benzene–light petroleum, short-path distillation, and recrystallisation gave a mixture of plates and needles, m. p. 105—106°.

9-*Methyl*-3 : 4-*benzophenanthridine*.—2-Acetamido-1-phenylnaphthalene (0·52 g.), phosphorus oxychloride (25 c.c.), and stannic chloride (0·75 g.) were refluxed for 2½ hr. 9-*Methyl*-3 : 4-*benzophenanthridine* was obtained as needles (0·42 g.), m. p. 105—107° (Found : C, 86·7; H, 5·7. $C_{18}H_{13}N,\frac{1}{3}H_2O$ requires C, 86·7; H, 5·5%). The *picrate*, m. p. 238° (decomp.) (Found : C, 60·2; H, 3·2. $C_{18}H_{13}N,C_6H_3O_7N_3$ requires C, 61·0; H, 3·4%), formed bright yellow needles from 2-ethoxyethanol.

7-*Methyl*-3 : 4-*benzophenanthridine*.—2-Formamido-1-*p*-tolylnaphthalene (0·1 g.), phosphorus oxychloride (5 c.c.), and stannic chloride (0·15 g.) were refluxed for 10 min. Processing as in the previous case gave an oil (0·05 g.) which provided the *picrate*, forming small yellow needles, m. p. 280° (decomp.) (Found : C, 62·5; H, 3·2. $C_{18}H_{13}N,C_6H_3O_7N_3$ requires C, 61·0; H, 3·4%), from 2-ethoxyethanol.

7 : 9-*Dimethyl*-3 : 4-*benzophenanthridine*.—As for the 9-methyl compound, 2-acetamido-1-*p*-tolylnaphthalene (0·43 g.), phosphorus oxychloride (30 c.c.), and stannic chloride (0·53 g.) provided 7 : 9-*dimethyl*-3 : 4-*benzophenanthridine*, which formed needles (0·36 g.), m. p. 96—98° (Found : C, 83·0; H, 6·3. $C_{19}H_{15}N,H_2O$ requires C, 82·9; H, 6·2%), from benzene–light petroleum. The *picrate*, m. p. 250° (Found : C, 61·4; H, 3·0%), gave yellow needles from the usual solvent.

2-*Methyl*-6-β-*naphthyliminomethyl*cyclo*hexanone*.—2-Hydroxymethylene-6-methyl*cyclo*-hexanone (1 g.), β-naphthylamine (1·02 g.), and ethanol (5 c.c.) were refluxed for 20 min. The anil separated on cooling and formed yellow needles (1·8 g.), m. p. 125—127°, from ethanol. When this was treated with formic acid in the usual way only a small amount of 2-formamidonaphthalene, m. p. 127—129°, was recovered.

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