Transformations of 2-Substituted 1-Dialkylaminoanthraquinones. A Re-investigation [1]

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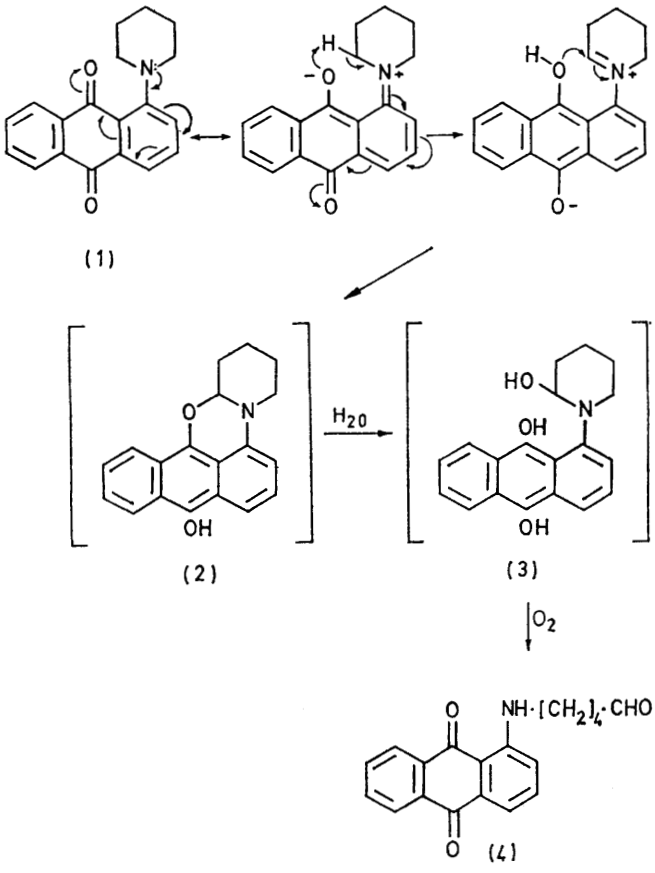
The thermal and photolytic transformations of 2-acylamino-1-dialkylaminoanthraquinones have been reinvestigated and shown to give in appropriate cases (i) *N*-acyldihydroimidazoanthraquinones and not 1-dialkylamino-2-oxaziridinylanthraquinones as suggested recently; or (ii) 1,2-dimethylimidazoanthraquinones and not 1-methylimidazoanthraquinones. The corresponding cyclisations of 2-amino-1-dialkylaminoanthraquinones give rise to two products: the imidazoanthraquinone and, surprisingly, 2-aminoanthraquinone. The reactions are rationalised mechanistically.

THE chemistry of *ortho*-substituted *NN*-dialkylanilines has recently been reviewed.[2] Frequently, unexpected products are obtained during simple reactions of these compounds. For example Fokin and his co-workers [3] observed dealkylation of various 1-dialkylaminoanthraquinones on heating at 160—190° in pyridine, a reaction originally reported by Bradley and his co-workers.[4] The Russian group extended this reaction to cyclic 1-aminoanthraquinones such as the piperidino-derivative (1), and again observed ring opening to give the aldehyde (4),[5] which they showed was formed by way of the intermediates (2) and (3) since (2) could be trapped as its acetate on treatment of the reaction mixture with acetic anhydride.[6] Our mechanistic rationale for this sequence is depicted in Scheme 1. Other related quinones have been shown to react in a similar manner under photolytic conditions.[7]

Fokin and his school have since then extended their research to the chemistry of 1-dialkylamino- (or polymethylenimino-) 2-acylaminoanthraquinones (5) and have unravelled three different types of reaction (Scheme 2): (A) isomerisation of the acylamino-group to give an oxaziridine (6);[8] (B) displacement of the 1-substituent by the acylamino-oxygen to give an oxazole (7);[9] and (C) cyclisation with displacement of the acyl group to give an imidazole (8).[9] The purpose of the present paper is to demonstrate that reactions (A) and (C) have been wrongly interpreted and in fact

[1] Preliminary communication, J. Lynch and O. Meth-Cohn, *Tetrahedron Letters*, 1970, 161.
[2] O. Meth-Cohn and H. Suschitzky, *Adv. Heterocyclic Chem.*, 1972, **14**, 211.
[3] E. P. Fokin and V. V. Russkikh, *Izvest. sibirsk. Otdel. Akad. Nauk, Ser. khim. Nauk*, 1965, 126.
[4] W. Bradley and E. Leete, *J. Chem. Soc.*, 1951, 2147; W. Bradley and R. F. Maisey, *ibid.*, 1954, 247.
[5] E. P. Fokin and V. V. Russkikh, *Zhur. org. Khim.*, 1966, **2**, 907 (*J. Org. Chem. U.S.S.R.*, 1966, **2**, 902).
[6] E. P. Fokin and V. V. Russkikh, *Zhur. org. Khim.*, 1966, **2**, 912 (*J. Org. Chem. U.S.S.R.*, 1966, **2**, 907).
[7] E. P. Fokin and E. P. Prudchenko, *Izvest. sibirsk. Otdel. Akad. Nauk, Ser. khim. Nauk*, 1966, 98; D. W. Cameron and R. G. F. Giles, *Chem. Comm.*, 1965, 573; *J. Chem. Soc.* (*C*), 1968, 1461; I. Baxter and D. W. Cameron, *J. Chem. Soc.* (*C*), 1968, 1747.
[8] E. P. Fokin and V. Ya. Denisov, *Zhur. org. Khim.*, 1968, **4**, 1486 (*J. Org. Chem. U.S.S.R.*, 1968, **4**, 1428).
[9] E. P. Fokin, V. Ya. Denisov, and L. N. Anishina, *Izvest. sibirsk. Otdel. Akad. Nauk, Ser. khim. Nauk*, 1970, **1**, 83.

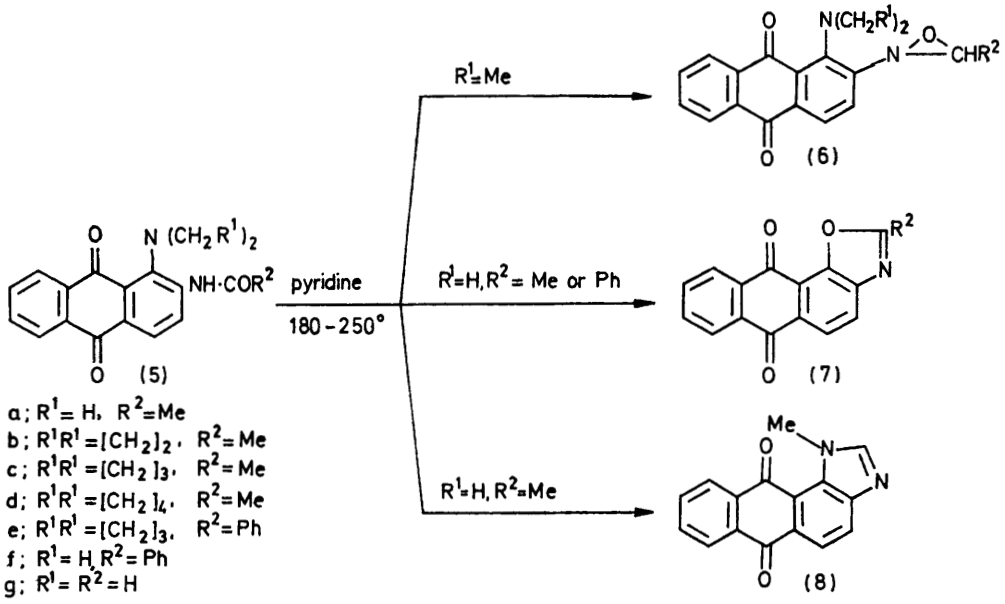


SCHEME 1

give different products, and to throw light on the mechanism of this whole area of chemistry.

In our hands the method employed by Fokin's group generally gave mixtures of products and we therefore used the method outlined in Scheme 3. 2-Aminoanthraquinone (9) is readily chlorinated with sulphuryl chloride in nitrobenzene to give mainly the 1-chloroderivative (10).[10] Small amounts of di- and tri-chloro-compounds are conveniently removed by chromatography after condensation with a suitable base. The condensation was best conducted in pyridine solution; low yields were obtained in the absence of solvent and other reactions occurred when, for example, dimethylformamide (DMF) was used as solvent. Thus with pyrrolidine in DMF, the dimethylamino-derivative (11a) was isolated rather than the expected product (11b), probably as a result of pyrrolidine reacting preferentially with the solvent and liberating dimethylamine. All the compounds reported herein are coloured and are readily observed in t.l.c. and column chromatography. Basic alumina was generally found to be preferable to silica since, with acyl derivatives, the latter often caused hydrolysis. Every compound was meticulously purified until it showed only one spot on t.l.c. with various solvent systems. Acylation of the amines (12) was conducted by standard methods to give the required materials (5). However, even this reaction can cause problems if not controlled carefully as shown later.

The identification of the oxaziridine (6) by Fokin was based upon i.r. spectral data (no NH or amidic CO stretching frequencies), chemical reactivity and an unambiguous synthesis by the reaction of peracetic acid on the anil (12).[8] However, the n.m.r. spectrum immediately refutes this structure. Thus the piperidino-derivative (5c) gives a product [supposedly (6)] in the

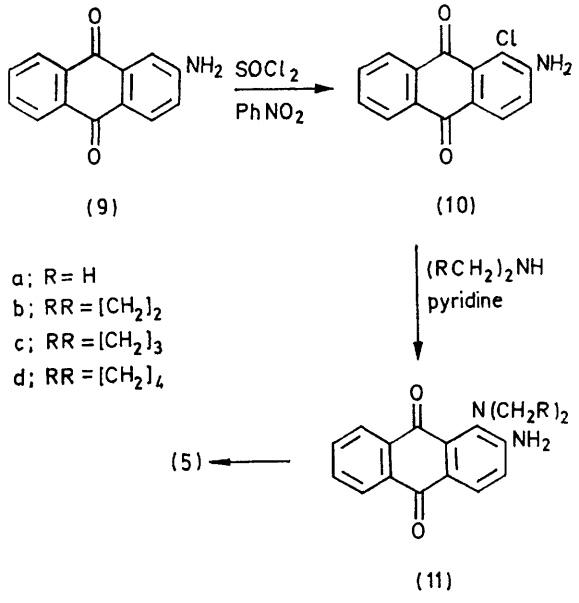


SCHEME 2

Since some of these observations may have been due to the use of impure materials, we first investigated the preparation of the appropriate starting materials (5). spectrum of which the methyl group appears as a singlet (rather than the expected doublet) and only nine other

[10] F.I.A.T. 1313, vol. II, p. 35.

aliphatic protons appear [rather than ten as for the oxaziridine (6c)]. Furthermore, three of the aliphatic protons gave distinct resonances at τ 4·35, 5·35, and 6·60, respectively, and an examination of their splitting pattern together with double resonance experiments allow them to be assigned to H-2(axial), H-6(equatorial), and H-6(axial), respectively, of a 1,2-disubstituted piperidine ring. Similar spectra are shown by the product from the benzoyl derivative (5e). The mass



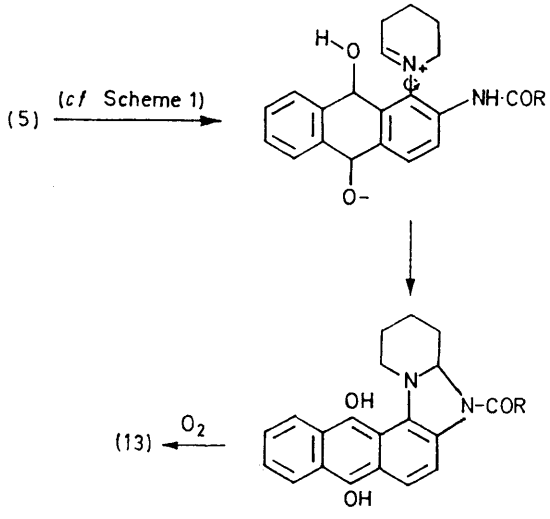
SCHEME 3

spectrum shows a molecular ion at *m/e* 408 [not 410 as expected for the oxaziridine (6e)] with a major loss of $M - 105$ (indicated by a metastable ion at *m/e* 225) corresponding to loss of PhCO, the base peak of the spectrum being due to $PhCO^+$, at *m/e* 105. On the foregoing evidence we now assign these products the structure (13), which though not isomeric with the oxaziridine (6) still is feasible on the ground of Fokin's elemental analyses. The apparent lack of an amide carbonyl absorption in the i.r. spectrum is due to masking of this peak by the anthraquinone absorption. Using the reaction conditions of Fokin's group we did not observe quantitative conversions of the acylamines (5) into the acyldihydroimidazoanthraquinones (13) and the mixture proved difficult to separate, p.l.c. being necessary. This fact could account for some of the reactions reported by Fokin, such as alkaline hydrolysis to the amine (11), reduction of supposed (6e) to the 2-benzylamino-derivative, and the action of ferric alum (apparently characteristic of oxaziridines) to give the 2-acylamino-compound, none of which we were able to reproduce on the pure compound (13).[8]

The ' unambiguous synthesis ' of the oxaziridine was also not reproducible in our hands. The Russian work reports use of ' 20% peracetic acid ' without specifying its formation and the nature of the solvent. However, we attempted this synthesis with three different mixtures of 20% peracetic acid each having a different amount of water–acetic acid as solvent. The products were carefully examined by t.l.c. and in one case separated quantitatively by p.l.c. to give a very low yield of the acyldihydroimidazoanthraquinone (13e) together with nine other products including benzaldehyde, benzoic acid, and 2-amino-1-piperidinoanthraquinone and its *N*-acetyl and *N*-benzoyl derivatives. No trace of the true oxaziridine could be detected. The ready acid-catalysed cyclisation of *NN*-disubstituted *o*-amino-anils to give dihydroimidazoles [11] could account for the trace of cyclised product.

We have applied this reaction to the corresponding 1-pyrrolidino- and 1-perhydroazepin-1-yl derivatives (5b and d) and in each case obtained initially the expected purple product [presumably (13)], which on chromatographic work-up underwent hydrolysis and oxidation to give the yellow imidazole (14a and c, respectively). In accord with the observations of Fokin the cyclisations of the acylamines (5) are equally well brought about by photolysis.[8] The imidazoles (14) are also available from oxidation of the amines (11) with performic acid [12] or from thermal or photolytic decomposition of the corresponding azide (11; N_3 for NH_2).

The formation of the acyldihydroimidazoanthraquinones (13) is rationalised in Scheme 4 in accord with



SCHEME 4

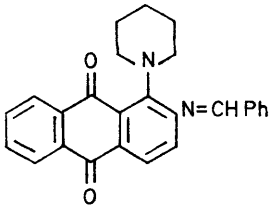
numerous analogous reactions of *ortho*-substituted *NN*-dialkyl anilines [2] and in particular with the reactions of 1-piperidinoanthraquinone (Scheme 1). That the last step takes place on opening the sealed tube to the atmosphere is evident in the rapid change of the reaction mixture from bright red to purple, in accord with similar proven observations of Fokin's group [5,6] (Scheme 1).

When this thermal transformation is attempted with the 1-dimethylamino-compounds (5a) it takes a com-

[11] R. K. Grantham and O. Meth-Cohn, *J. Chem. Soc.* (*C*), 1969, 1444.

[12] *Cf.* E. P. Fokin and V. Ya. Denisov, *Khim. geterotsikl. Soedinenii*, 1970, 321.

pletely different course. Fokin's group indicated that the benzoyl derivative (5f) underwent displacement of the dimethylamino-group and cyclisation of the acyl function to give the oxazole (7f) in 92% yield, while the acetyl derivative (5a) gave the corresponding oxazole (7a) (17·5%) and the imidazole (8) (23·5%), the latter structure again being supported by i.r. evidence and an unambiguous synthesis.[9] The oxazole formation has a number of analogies in the literature.[13] However, the formation of the imidazole seemed surprising to us. In our hands under identical reaction conditions but with p.l.c. work-up, the 2-acetylamino-1-dimethylamino-anthraquinone (5a) gave the starting material, together with the reported oxazole (7a) and the dimethylimidazole (14d), but no monomethylimidazole (8). It is difficult to explain this difference. The monomethyl derivative melts at 254° whereas the dimethyl compound melts at 198°. Both are readily prepared and though their i.r. spectra are similar they are easily distinguished. It is of



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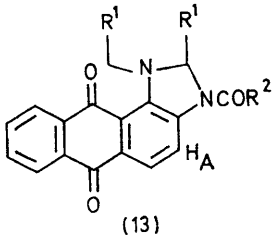
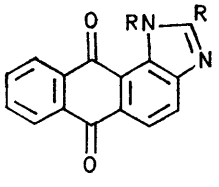


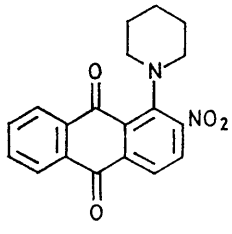
(13)

R^1 and R^2 as in (5)



(14)

a; RR = $[CH_2]_3$
b; RR = $[CH_2]_4$
c; RR = $[CH_2]_5$
d; R=Me



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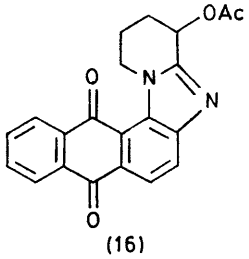

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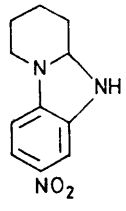
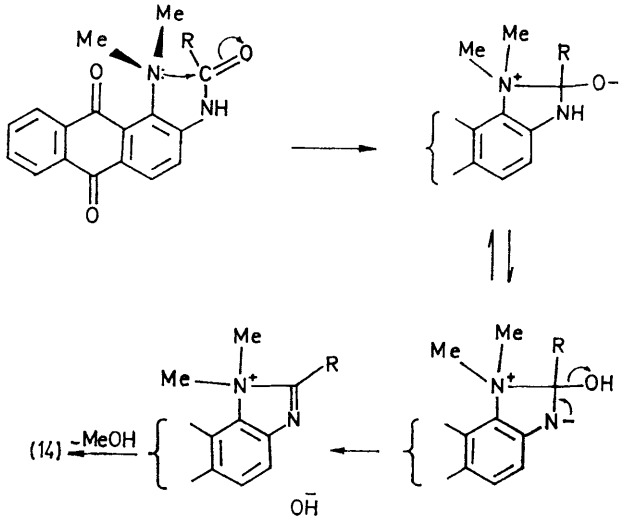


(17)

interest that prolonged refluxing of 2-amino-1-dimethylaminoanthraquinone (11a) in acetic anhydride (20 min) produces the 1,2-dimethylimidazoanthraquinone (14d) in accord with the observations of Pinnow.[2] Photolysis of the acetylamino-derivative (5a) gives a complex mixture of thirteen compounds from which the same oxazole (7a) and dimethylimidazole (14d) may be



SCHEME 5

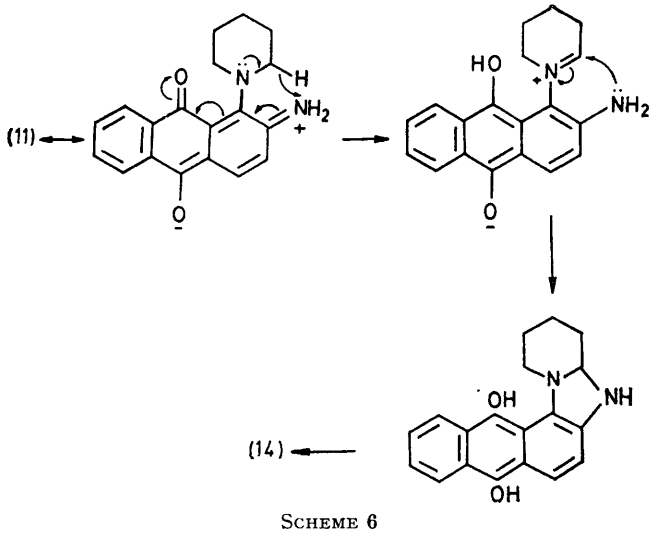
isolated by p.l.c. The formation of this dimethylimidazole may be best rationalised by analogy with the mechanism of the Pinnow reaction [2] (Scheme 5).

The foregoing three modes of reaction of the acylamines (5) may be seen as attack of the 2-substituent (i) at the dialkylamine α-position to give (13), (ii) at the 1-nitrogen atom to give (14), or (iii) at C-1 of the anthraquinone to give (7). Formation of the acyldihydroimidazoanthraquinone (13) requires the dialkylamino-group to be coplanar with the aromatic ring (in order for mesomerism with the CO groups to occur—see Scheme 1) whereas the oxazole (7) and 1,2-dimethylimidazole (14d) formation probably involves an orthogonal 1-substituent. Furthermore, the bulkier the acyl group, the less favoured should imidazole formation be compared with oxazole formation, since the former involves the acyl group being coplanar with the ring, with its substituent directed towards the 1-substituent (see Scheme 5). Thus, the bulkier the 1-substituent the less likely is reaction resulting in (13), whereas the larger the acyl substituent the more likely should oxazole formation be.

To test this hypothesis we prepared the formyl derivative (5g) in which the bulky dimethylamino-group remains but a much smaller acyl substituent is present. The compound was heated in pyridine in the usual way and gave a mixture of the formyldihydroimidazoanthraquinone (13 g) and the imidazole (8) but no oxazole, thus supporting the foregoing ideas. However, oxazole formation appears to occur in the mass spectrometer: the base peak of the formyl compound (5 g) corresponds to loss of dimethylamine.

[13] F. Ullman and W. Junghans, *Annalen*, 1913, **399**, 335; M. Fries and P. Ochwat, *Ber.*, 1923, **56**, 1291; Ger.P. 286,093 and 286,094/1915 (*Chem. Zentr.*, 1915, **3**, 567); F. I. Carrol and J. T. Blackwell, *Chem. Comm.*, 1969, 923.

The attack of the 2-substituent at the α-position should be even readier with the more nucleophilic and less sterically hindered amine (11) rather than its acyl derivative (5). This was indeed found to be the case but a curious, and as yet unexplained reaction was revealed. Heating the amines (11) in pyridine brought about their conversion into the corresponding imidazoles (14) together with the formation of 2-aminoanthraquinone (9), in each case in the molar proportion of roughly 2 : 1 as judged by their n.m.r. spectra. Our first idea as to the source of the latter product was in terms of the action of an intermediate dihydroimidazole (such materials are known to be powerful reducing agents and sources of hydride ions [14]) on the starting material. However, the action of a dihydroimidazole (17), sodium borohydride in refluxing bis-(2-methoxyethyl) ether, or sodium bis(methoxyethoxy)aluminium hydride in hot toluene failed to produce 2-aminoanthraquinone from the amine (11c). Furthermore, irradiation of the amines (11) under either nitrogen or oxygen gave no amine (9), but only the imidazoles (14), suggesting that a different type of mechanism accompanied the photo-reaction. In this case the reaction probably proceeds in a manner analogous to the known photocyclisations of quinone imines to imidazoles as proposed in Scheme 6.[7]



SCHEME 6

Finally, heating the nitro-compound (15) in pyridine gave the imidazole (14) together with several unidentified by-products; treatment of the same nitro-compound with zinc chloride and acetic anhydride gave the expected [15] α-acetoxylated imidazole (16).

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257, n.m.r. spectra on a Varian A60A or HA100, and mass spectra on an A.E.I. MS12 instrument. For u.v. irradiation a high-pressure mercury lamp (Q81, Quartzlampen, GMBH, Hanau) with a Pyrex water cooling jacket was used.

2-Amino-1-chloroanthraquinone was prepared according to a F.I.A.T. method,[10] 2-aminoanthraquinone (100 g) yielding the required product (95·5 g, 83%), m.p. 238°.

1-*Chloro*-2-*nitroanthraquinone*.—Hydrogen peroxide (90%; 7 ml) was added to ice-cooled chloroform (70 ml) with stirring followed dropwise by trifluoroacetic acid (48 ml). After a further 15 min at 0—5° the mixture was heated to reflux and a suspension of 2-amino-1-chloroanthraquinone (6·9 g) in chloroform (100 m), was added during 15 min. After 1 h under reflux, water (50 ml) was added and the chloroform was evaporated. The resulting precipitate was filtered off, water-washed, and dried. Recrystallisation (benzene–chlorobenzene, 3 : 1) gave the nitro-compound (6·0 g, 80%), m.p. 258° (lit.,[16] 258°).

Condensation of 2-*Amino*-1-*chloroanthraquinone with Bases*.—The anthraquinone (0·02 mol), the amine (0·05 mol), and pyridine (20 ml) were heated under reflux for 24 h. (In the case of dimethylamine the reaction was conducted in a sealed tube at 110°.) The resulting mixture was poured into water and the precipitate filtered off, water-washed, and dried. The solid was dissolved in chloroform and adsorbed onto alumina (~10 times its weight) and the dry material chromatographed on alumina in benzene. The first band (yellow) gave a small amount of polychlorinated impurities present in the starting material. The second, dark red band gave the required amines (11): (*a*) 2-amino-1-dimethylaminoanthraquinone (11a) (63%), needles from benzene–light petroleum, m.p. 178° (lit.,[9] 177—178°), τ (CDCl$_3$) 5·0br (NH$_2$), 7·16 (s, Me), and 1·6—3·1 (m, aromatic); (*b*) 2-*amino*-1-*pyrrolidin*-1-*ylanthraquinone* (11b) (46%), needles from benzene–light petroleum, m.p. 166—167° (Found: C, 74·0; H, 5·6; N, 9·5. $C_{18}H_{16}N_2O_2$ requires C, 74·0; H, 5·5; N, 9·6%), τ (CDCl$_3$) 4·9br (NH$_2$), 6·82 (m, CH_2·N·CH_2), 7·87 (m, $[CH_2]_2$), and 1·6—3·0 (m, aromatic); (*c*) 2-*amino*-1-*piperidinoanthraquinone* (11c) (60%), as needles from benzene–light petroleum, m.p. 174° (lit.,[8] 174—175°), τ (CDCl$_3$) 4·96br (NH$_2$), 7·00 (m, CH_2·N·CH_2), 8·30 (m, $[CH_2]_3$), and 1·6—3·05 (m, aromatic); (*d*) 2-*amino*-1-*perhydroazepin*-1-*ylanthraquinone* (11d) (38%), needles from benzene–light petroleum, m.p. 150—152° (Found: C, 74·8; H, 6·4; N, 8·4. $C_{20}H_{20}N_2O_2$ requires C, 75·0; H, 6·4; N, 8·7%), τ (CDCl$_3$) 4·84br (NH$_2$), 6·75 (m, CH_2·N·CH_2), 8·15 (m, $[CH_2]_4$), and 1·6—3·0 (m, aromatic).

Acetylation of the 2-*Aminoanthraquinones* (11).—The amine (0·01 mol) in acetic anhydride (5 ml) was heated on a steam-bath for 5 min. Water (30 ml) was then added and heating was continued for a further 5 min. After cooling the orange products were filtered off, dried, and recrystallised from benzene–light petroleum to give needles in very high yield: (*a*) 2-acetylamino-1-dimethylaminoanthraquinone (5a), m.p. 160° (lit.,[9] 159—160°), τ (CDCl$_3$) 0·76br (NH), 1·15 (d, *J* 9·0 Hz, H-3), 1·6—2·5 (m, aromatic), 7·13 (s, NMe_2), and 7·72 (s, Ac) {prolonged refluxing (20—30 min) of the amine with acetic anhydride gave a product which on chromatography on an alumina column with benzene as eluant gave first the yellow, 1,2-*dimethylimidazo*[4,5-a]*anthraquinone* (14d), m.p. 198° (see Table 1) followed by the acetyl derivative}; (*b*) 2-*acetylamino*-1-*pyrrolidin*-1-*ylanthraquinone* (5b), m.p. 168° (Found: C, 71·8; H, 5·6; N, 8·1. $C_{20}H_{18}N_2O_3$ requires C, 71·85; H, 5·4; N, 8·4%), τ (CDCl$_3$) 0·6br (NH), 1·20 (d, *J* 9·0 Hz, H-3), 1·70—2·50 (m, aromatic), 6·80br (N·CH_2's), and

[14] *E.g.* R. K. Grantham, O. Meth-Cohn, and M. A. Naqui, *J. Chem. Soc.* (*C*), 1969, 1438.

[15] R. K. Grantham and O. Meth-Cohn, *J. Chem. Soc.* (*C*), 1969, 70.

[16] E. Kopetschni, Ger.P. 363,930/1924 (*Chem. Abs.*, 1924, **18**, 991).

7·73br (CH_2·CH_2 and CH_3); (*c*) 2-acetylamino-1-piperidinoanthraquinone (5c), m.p. 222° (lit.,[8] 222—222·5°), τ ($CDCl_3$) 0·6br (NH), 1·15 (d, *J* 8·5 Hz, H-3), 1·6—2·35 (m, aromatic), 7·00br (N·CH_2's), 7·73 (s, Me), and 8·26br ([CH_2]$_3$); (*d*) 2-*acetylamino*-1-*perhydroazepin*-1-*ylanthraquinone* (5d), m.p. 168° (decomp.) (Found: C, 72·8; H, 5·9; N, 7·55. $C_{22}H_{22}N_2O_3$ requires C, 72·9; H, 6·1; N, 7·7%), τ ($CDCl_3$) 0·3br (NH), 1·15 (d, *J* 8·5 Hz, H-3), 1·6—2·65 (m, aromatic), 6·85br (N·CH_2's), 7·70 (s, Me), and 8·20br ([CH_2]$_4$).

2-*Benzoylamino*-1-*piperidinoanthraquinone* (5c).—2-Amino-1-piperidinoanthraquinone (11c) (3·06 g, 0·01 mol) in pyridine (10 ml) was treated with benzoyl chloride (7·0 g, 0·05 mol). The mixture was heated on a water-bath for 15 min, then poured onto ice (50 ml). The yellow precipitate was filtered off, washed with water, dried, and recrystallised from chlorobenzene to give 2-benzoylamino-1-piperidinoanthraquinone (5e) (3·6 g, 90%), m.p. 224° (lit.,[8] 222—224°).

1-*Dimethylamino*-2-*formylaminoanthraquinone* (5g).—2-Amino-1-dimethylaminoanthraquinone (0·2 g) in formic acid (98—100%; 2·0 ml) and acetic anhydride (0·5 ml) was heated under reflux for 20 min. The mixture was poured into water (20 ml) and the yellow precipitate filtered off, washed with water, and dried. Recrystallisation from chlorobenzene gave the *formyl derivative* as golden needles (0·22 g, 100%), m.p. 239—240° (Found: C, 69·3; H, 4·7; N, 9·4. $C_{16}H_{14}N_2O_2$ requires C, 69·4; H, 4·8; N, 9·5%), $\nu_{max.}$ (Nujol) 3295 (NH), 1710 (CHO), and 1680 cm^{-1} (CO), *m/e* 294 (M^+, 61%), 266 (*M* — CO, 80%, *m** 240·7), and 249 (*M* — Me_2NH, 100%).

2-*Nitro*-1-*piperidinoanthraquinone* (15).—1-Chloro-2-nitroanthraquinone (6·0 g), piperidine (5 ml), and chloroform (20 ml) were heated under reflux for 24 h. The solvent and excess of piperidine were removed under vacuum and the residue was treated with water and extracted with benzene. The benzene layer was water-washed, dried ($MgSO_4$), and adsorbed onto activated alumina by evaporation. The adsorbate was added to an alumina column and eluted with benzene, giving first a small amount of chloronitroanthraquinone, followed by the title product as a red band. The red solid crystallised from benzene–light petroleum (1 : 1) as red needles, m.p. 196° (Found: C, 67·7; H, 4·85; N, 8·3. $C_{19}H_{16}N_2O_4$ requires C, 67·85; H, 4·8; N, 8·3%), τ ($CDCl_3$) 1·70—2·26 (aromatic), 6·90br (N·CH_2's), and 8·33br ([CH_2]$_3$), *m/e* 336 (M^+, 23%) and 319 (*M* — OH 100%; *m** 303).

2-*Azido*-1-*piperidinoanthraquinone*.— 2-Amino-1-piperidinoanthraquinone (2·5 g) was added with stirring to hydrochloric acid (36% w/v; 30 ml) and water (15 ml). The slurry was cooled to 0° and sodium nitrite (1·5 g) in the minimum amount of water was added dropwise with stirring. The mixture was stirred for 10 min and then added slowly to a stirred solution of sodium azide (5 g) and sodium acetate (60 g) in water (200 ml) at room temperature. The precipitate was filtered off, washed with water, dried, and chromatographed on a silica column. Elution with benzene gave some unchanged material; elution with chloroform gave the *azide* (1·65 g, 64%) as dark red crystals, m.p. 126° (decomp.) (Found: C, 68·6; H, 5·0; N, 16·6. $C_{19}H_{16}N_4O_2$ requires C, 68·7; H, 4·85; N, 16·9%), $\nu_{max.}$ (Nujol) 2120 cm^{-1} (N_3), τ ($CDCl_3$) 1·6—2·65 (m, aromatic), 6·90br (N·CH_2's), and 8·28br ([CH_2]$_3$), *m/e* 332 (M^+, 11%), 304 (*M* — N_2, 75%), and 275 (100%).

2-*Benzylideneamino*-1-*piperidinoanthraquinone* (12).—2-Amino-1-piperidinoanthraquinone (5·0 g) and benzaldehyde (2 ml) in toluene (50 ml) were heated under reflux for 16 h under a Dean–Stark head. The volume was reduced to 20 ml by distillation and, on cooling, the solution precipitated the title compound, which gave red needles (from chlorobenzene), m.p. 211° (lit.,[8] 211—212°).

Peracetic Acid Oxidation of 2-*Benzylideneamine*-1-*piperidinoanthraquinone*.—(*a*) The anil (0·2 g) in pyridine (60 ml) was treated dropwise with a mixture of acetic acid (3 ml) and hydrogen peroxide (30%; 7 ml) [to which had been added sodium hydrogen carbonate (0·5 g) 1 h after mixing]. The reaction was continued as described by Fokin and Denisov, and the residue was chromatographed on 1 mm thick silica plates (20 × 20 cm) with benzene as eluant, six elutions being necessary. By this means the following bands were isolated (in order of mobility): (i) benzaldehyde, (ii) benzoic acid, (iii) and (iv) unidentified traces, (v) 2-benzoylamino-1-piperidinoanthraquinone (0·03 g), (vi) 2-2-amino-1-piperidinoanthraquinone (0·11 g), (vii) the benzoyldihydroimidazoanthraquinone (13e) (trace), (viii) 2-acetylamino-1-piperidinoanthraquinone (0·02 g), and (ix) unidentified material.

(*b*) To the anil (0·1 g) in pyridine (25 ml) was added a mixture of hydrogen peroxide (90%; 1·3 ml) and acetic anhydride (3·7 ml), dropwise at room temperature. Work-up as in (*a*) gave similar products but much more 2-benzoylamino-1-piperidinoanthraquinone and less of the other products.

(*c*) The oxidation was conducted as in (*a*) with 1 ml of water added to the peracetic acid solution. The same products were formed as in (*a*), in similar proportions.

Thermal Transformations of the Acylamines (5) *and Amines* (11).—The amine or acylamine in dry pyridine (distilled from barium oxide; 4 ml per g of solid) was heated in a sealed glass tube at 180° for 12 h. The cooled contents were poured into water (100 ml per 4 ml of pyridine) and the precipitate was filtered off, washed, dried, and chromatographed on alumina. The properties of the products are shown in Tables 1 and 2.

Irriadiation of 2-*Amino- and* 2-*Acylamino-anthraquinones*.—The appropriate compound [(5) or (11)] as a 1% solution in benzene was irradiated until starting material was absent or minimal, as shown by t.l.c. when the solvent was removed and the residue recrystallised. By this means the following products were prepared. (*a*) From 2-amino-1-pyrrolidin-1-ylanthraquinone (11b) was obtained the corresponding imidazole (14a), m.p. 266° (70%); (*b*) from 2-amino-1-piperidinoanthraquinone (11c) was obtained the imidazole (14b) (66%), m.p. 250°; (*c*) from 2-acetylamino-1-piperidinoanthraquinone (5e) was obtained the acyldihydroimidazole (13c) (80%), m.p. 173°; (*d*) from 2-benzoylamino-1-piperidinoanthraquinone (5e) was obtained the acyldihydroimidazole (13e) (77%), m.p 208°; (*e*) from 2-acetylamino-1-pyrrolidin-1-ylanthraquinone (5b) was obtained the imidazole (14a) (70%), m.p. 266°; (*f*) from 2-acetylamino-1-perhydroazepin-1-ylanthraquinone (5d) was obtained the imidazole (14c) (74%), m.p. 192—194°; (*g*) from 2-acetylamino-1-dimethylaminoanthraquinone (5a) was obtained the imidazole (14d) (29%), m.p. 198°, together with the oxazole (7a) (21%), m.p. 212—213°.

Decomposition of 2-*Azido*-1-*piperidinoanthraquinone*.—(i) The azide (1·65 g) in bis-(2-methoxyethyl) ether (20 ml) was heated at 165° until nitrogen evolution ceased (10 min). The solvent was removed under vacuum and the residue chromatographed on alumina in benzene–chloroform (1 : 1) to give the imidazole (14b) (1·2 g, 73%).

(ii) Irradiation of a 1% solution of the azide (1·65 g) in benzene under nitrogen or oxygen gave the same imidazole (14b) (1·3 g, 80%).

Thermal and Photo-reactions of 2-Nitro-1-piperidinoanthraquinone (15).—The nitro-compound (0·45 g) in dry pyridine (3 ml) was heated at 150° in a sealed tube for 6 h. The cooled solution was poured into water and the precipitate filtered off, water-washed, dried, and chromatographed on alumina. Elution with benzene–chloroform and dried. Recrystallisation from chlorobenzene gave 4-*acetoxy*-1,2,3,4-*tetrahydroanthra*[2,1-d]*pyrido*[1,2-a]*imidazole*-8,13-*quinone* (16) (0·4 g, 53%) as golden needles, m.p. 217—218° (Found: C, 69·6; H, 4·7; N, 7·5. $C_{21}H_{16}N_2O_4$ requires C, 70·0; H, 4·5; N, 7·8%), $\nu_{max.}$ (Nujol) 1740 (CO_2) and 1680 cm^{-1} (CO), τ ($CDCl_3$) 1·65—2·50 (m, aromatic), 3·80 (m, CH), 5·34 (m, N·CH_2), 7·85 (s, Me), and 7·96 (m, $[CH_2]_3$), *m/e* 360 (M^+, 5%) and 317 (M — CH_3CO, 100%, *m** 279).

TABLE 1

Properties of the products derived from heating the acylamines (5) or amines (11) in pyridine

Substrate	Product	Yield (%)	M.p. (°C)	Found (%) C	Found (%) H	Found (%) N	Formula	Required (%) C	Required (%) H	Required (%) N
(5a)	(14d)	21	198	72·8	4·6	10·4	$C_{16}H_{12}N_2O_2$	72·7	4·6	10·6
	(7d)	20	212—213 [a]							
(5b)	(14a)	68	266	74·5	4·3	9·8	$C_{18}H_{12}N_2O_2$	75·0	4·2	9·7
(5c)	(13c)	73	173 [b]							
(5d)	(14c)	65	192—194 *	75·6	5·15	8·5	$C_{20}H_{16}N_2O_2$	75·9	5·1	8·9
(5e)	(13e)	66	208 [c]							
(5g)	(13g)	10	179	69·4	4·0	9·3	$C_{16}H_{12}N_2O_3$	69·8	4·1	9·6
	(8)	15	254 [c]	73·6	4·2	10·4	$C_{16}H_{10}N_2O_2$	73·25	3·8	10·7
(11a)	(8) [d]	High	254 [e]							
(11b)	(14a) [d]	High	266 *							
(11c)	(14b) [d]	High	250 [f]							
(11d)	(14c) [d]	High	192—194 *							

* Decomp.

[a] Lit.,[9] m.p. 209—212°. [b] Lit.,[8] m.p. 170—171°. [c] Lit.,[9] m.p. 207—209°. Together with 2-aminoanthraquinone (molar ratio 2 : 1). [d] Lit.,[9] 253—255°. [e] Lit.,[12] m.p. 250—252°.

TABLE 2

Spectral data for the acyldihydroimidazoanthraquinones (13)

Compound	τ ($CDCl_3$)	*m/e*
(13c)	1·6—2·5 (m, aromatic), 4·35 (m, H-2*ax*),* 5·35br (d, H-6*eq*),* 6·62 (m, H-*ax*),* 7·68 (s, Me), and 7·85—8·8 (m, $[CH_2]_3$) *	346 (M^+)
(13e)	1·6—2·7 (m, aromatic), 3·23 (d, *J* 8·5 Hz, H-3), 4·1—4·4 (m, N·CH_{ax}), 5·15—5·6 (N·CH_{2eq}), 6·4—7·0 (m, N·CH_{2ax}), 7·5—8·85br (m, $[CH_2]_3$)	408 (35%; M^+), 303 (70%; M — COPh; *m** 225), 105 (100%; PhCO)
(13g)	1·11 (s, CHO), 1·7—3·0 (m, aromatic), 4·70 (s, N·CH_2·N), 6·90 (s, NMe)	292 (50%; M^+, 263) (100%; M — CHO; *m** 236·8)

* Piperidine ring protons. † See ref. 1 for reproduction of spectrum.

(1 : 1) gave first starting material (0·15 g), followed by the imidazole (14b) (0·05 g, 12%). Irradiation of the same nitro-compound in benzene was without effect even after 300 h. Irradiation in aqueous methanolic hydrochloric acid or heating for 100 h in constant-boiling hydrochloric acid also caused no change.

Action of Acetic Anhydride and Zinc Chloride on 2-Nitro-1-piperidinoanthraquinone.—The nitro-compound (0·7 g), zinc chloride (0·24 g), and acetic anhydride (20 ml) were boiled for 6 h. The product was then poured into water (200 ml) and the precipitate filtered off, washed with water,

Peracid Oxidation of 2-Amino-1-piperidinoanthraquinone.—The amine (0·35 g) was treated successively with formic acid (98—100%; 10 ml) and hydrogen peroxide (30%; 5 ml) and heated on a steam-bath for 15 min. After the exothermic reaction had subsided the mixture was poured into water (100 ml) and the precipitate filtered off, washed with water, and dried. Recrystallisation of the yellow solid from chlorobenzene gave the imidazole (14b) (0·2 g, 57%) as needles, m.p. 250°.

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