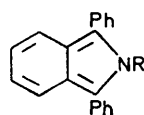# Autoxidation of Polysubstituted Isoindoles. Part II.[1] Products from 1,3-Diphenyl- and 1,2,3-Triphenyl-isoindoles

By Munir Ahmed, Larry J. Kricka, and John M. Vernon,* Department of Chemistry, University of York, Heslington, York YO1 5DD

2-(α-Iminobenzyl)benzophenones are obtained by autoxidation of 1,2,3,4,7-pentasubstituted isoindoles in which phenyl groups occupy the 1- and 3-positions. Where the isoindole 2-position also bears a phenyl group, the autoxidation is achieved under u.v. irradiation and the corresponding imine reacts further to give a phenanthridine derivative. Where the isoindole 2-position is unsubstituted, autoxidation products are 1-oxy-substituted 1H-isoindole derivatives.

SOME N-substituted 1,3,4,7-tetramethylisoindoles are autoxidised to the corresponding phthalimides.[1] The same free radical mechanism which accounts[1] for the loss of methyl groups from the 1- and 3-positions was also proposed to explain an analogous autoxidative demethylation in the pyrrole series.[2] Other types of autoxidation products are obtained from isoindoles with a different substitution pattern.[3]

Isoindoles stabilised by aryl substituents are much less easily autoxidised, although 2-methyl-1,3-diphenyl-isoindole (1) is oxidised in air to o-dibenzoylbenzene (4).[4] 1,2,3-Triphenylisoindole (2) reacts photochemically with oxygen to give the cyclic peroxide (3), which is hydrolysed to the same diketone (4).[5] We report here some new products obtained by autoxidation of the
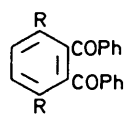

(1) R = Me
(2) R = Ph
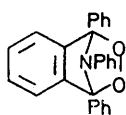
(3)

(4) R = H
(5) R = Me

triphenylisoindole (2) and of other isoindoles (6)—(9) which also contain 1- and 3-phenyl substituents.

Autoxidation of 4,7-dimethyl-1,3-diphenylisoindole (6) by passage of oxygen through a refluxing solution in tetrahydrofuran led to a crystalline product, m.p. 159—161°, which gradually changed into a second material, m.p. 217—218°. On the evidence of its oxidation of acidified potassium iodide solution and its i.r. and mass spectra (see Experimental section), the first product is believed to be the hydroperoxide (10). The pattern in the low-field region of the n.m.r. spectrum is inappropriate for a symmetrical structure, as of a cyclic peroxide analogous to (3).

The second product, which was also obtained from the first by reduction with sodium sulphite, was the 1-hydroxy-1H-isoindole (11). The corresponding com-

pounds (12) and (13) obtained from 1,3,4,7-tetramethyl-isoindole with oxygen or air, respectively, were characterised by Bonnett et al.,[6] and another hydroperoxide
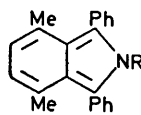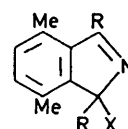

(6) R = H
(7) R = Me
(8) R = CH₂Ph
(9) R = Ph

(10) R = Ph, X = O·OH
(11) R = Ph, X = OH
(12) R = Me, X = O·OH
(13) R = Me, X = OH

analogous to (10) is the product of dye-sensitised autoxidation of 2,3,4,5-tetraphenylpyrrole.[7] The formation of compound (10) most likely occurs via a free-radical mechanism, although an ene reaction of the isoindole (6) or rearrangement of its cyclic peroxide are also conceivable (cf. ref. 7).

When solutions of the N-substituted isoindoles (7) and (8) were oxygenated in the same way, only oils were obtained. However, g.l.c. analysis indicated that these oils each consisted predominantly of one volatile component, and these products were assigned the corresponding imine structures (14) and (15) on the following evidence. The compounds showed i.r. absorptions appropriate to both C=O and C=N bonds, and they were separately hydrolysed by dilute acid to give 2,3-dibenzoyl-p-xylene (5), which could be obtained independently from the isoindole (6) with nitrous acid.[8] Accurate mass measurements confirmed the appropriate molecular formulae of (14) and (15), containing only one oxygen atom more than the isoindole from which each imine was derived.

In the expectation that the more conjugated N-phenylimines (16) and (17) might be crystalline, less susceptible to hydrolysis, and so more amenable to thorough characterisation, we examined the autoxidation

[1] Part I, L. J. Kricka and J. M. Vernon, J. Chem. Soc. (C), 1971, 2667.
[2] G. B. Quistad and D. A. Lightner, J.C.S. Chem. Comm., 1972, 116.
[3] J. D. White and M. E. Mann, Adv. Heterocyclic Chem., 1969, 10, 113.
[4] W. Theilacker and W. Schmidt, Annalen, 1955, 597, 95.

[5] W. Theilacker and W. Schmidt, Annalen, 1957, 605. 43.
[6] C. O. Bender, R. Bonnett, and R. G. Smith, J. Chem. Soc. (C), 1970, 1251.
[7] C. Dufraisse, G. Rio, A. Ranjon, and O. Pouchot, Compt. rend., 1965, 261, 3133.
[8] H. Fletcher, Tetrahedron, 1966, 22, 2481.

of the 1,2,3-triphenylisoindoles (2) and (9). The iso-indole (2) was apparently unchanged by passage of oxygen through a solution in refluxing toluene, and it was also photostable in the complete absence of oxygen. However, u.v. irradiation of a solution in dichloromethane in the presence of oxygen resulted in its rapid disappearance and the successive formation of two new products. Previous workers [5] had obtained the peroxide (3) under these conditions (although less cleanly in dichloromethane than in carbon disulphide as solvent), but our first product, m.p. 86—89°, arising after a few minutes irradiation, was instead the desired anil (17), as shown by elemental analysis, appropriate spectroscopic evidence, and hydrolysis to o-dibenzoylbenzene (4) and aniline. The presence of both C=N and C=O i.r. absorptions (1620 and 1660 cm⁻¹, respectively), and of important mass spectral peaks due to $PhCO^+$, $PhC\equiv\overset{+}{N}Ph$, and $o\text{-}PhCO\cdot C_6H_4\cdot C\equiv\overset{+}{N}Ph$ are consistent with the structure (17).

U.v. irradiation of the isoindole (8) in dichloromethane with bubbling oxygen gave small amounts of benzaldehyde, presumably derived from the N-benzyl

(14) R = Me
(15) R = CH₂Ph
(16) R = Ph

(17) R = COPh
(18) R = H
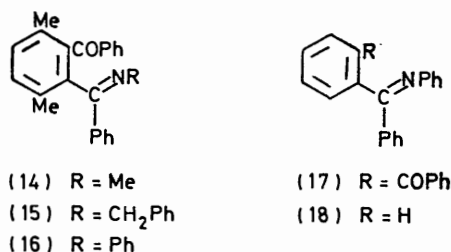
group, but no other recognisable products. Autoxidation of the isoindole (9) under the same conditions gave the corresponding anil (16), m.p. 141—142°, after only a few minutes irradiation. The n.m.r. spectrum of this product (16) shows that the two methyl groups are non-equivalent (τ 7·91 and 8·02). In the mass spectrum the prominence of peaks due to nitrilium ions, $ArC\equiv\overset{+}{N}Ph$, reflects the same fragmentation pattern of the molecular ion as found for the imines (14) and (17). The structure (16) is further confirmed by acidic hydrolysis to the diketone (5).

Since molecular oxygen is the source of the single oxygen atom in each of the imines (14)—(17), mechanistic steps involving O–O bond fission and reduction are implicated. In view of the isolation of the cyclic peroxide (3) from 1,2,3-triphenylisoindole (2),[5] and the implication of such peroxides in other autoxidation reactions,[1,2,4,9] it is likely that they are intermediates in the autoxidation of the isoindoles (7)—(9). The formation of imines is precedented by a previous result in the pyrrole series: [9] the dye-sensitised autoxidation of pentaphenylpyrrole in presence of acid gives an isolable 2-hydroxy-2H-pyrrolium salt (19), which de-

composes to give the imine (20) and thence the lactam (21) (Scheme 1). However, since the autoxidation of

(21)   (20)   (19)
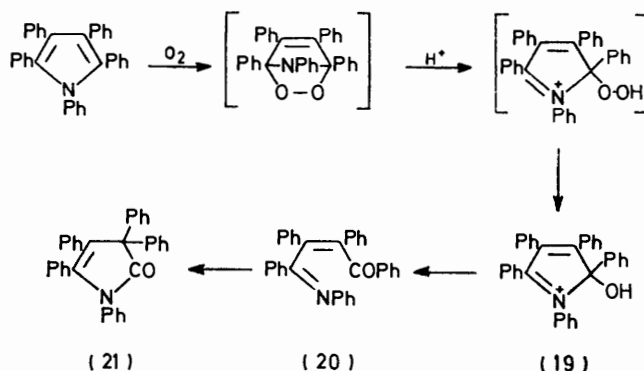
SCHEME 1

isoindoles occurs in the absence of acid, a more likely route to explain the formation of the imines (14)—(17) is that shown in Scheme 2.

This Scheme is similar to that proposed for the autoxidation of other polysubstituted isoindoles,[1] except that the formation of phthalimides is inhibited by the more difficult loss of phenyl instead of methyl radicals in the breakdown of the intermediate peroxide (cf. the formation of acetophenone rather than acetone in the decomposition of α-cumyloxyl radicals [10]). In order to obtain evidence in support of the Scheme, the peroxide (3) was heated in dichloromethane. The diketone (4) was thereby obtained, together with a second product which, although melting at a higher temperature than the anil (17), was identical with the latter with respect to i.r. spectrum and chromatographic behaviour. Presumably the O–O bond homolysis (step 2 in Scheme

(7)—(9)

(14)—(16)
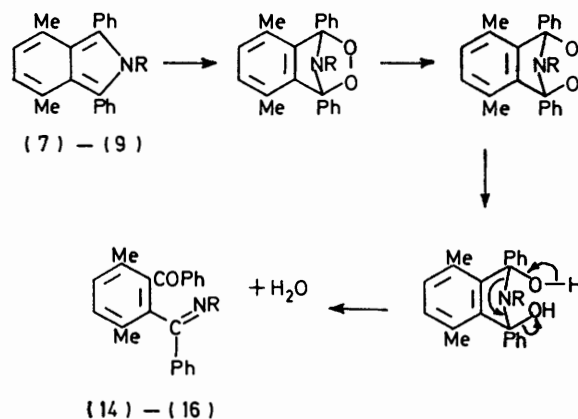
SCHEME 2

2) may occur thermally or photochemically. The absence of abstractable hydrogen atoms in carbon

[9] C. Dufraisse, G. Rio, and A. Ranjon, Compt. rend., 1967, 265, 310; G. P. Gardini. Adv. Heterocyclic Chem., 1973, 15, 67.

[10] M. S. Kharasch, A. Fono, and W. Nudenberg, J. Org. Chem., 1951, 16, 105; H. C. Bailey and R. G. W. Norrish, Proc. Roy. Soc. (A), 1952, 212, 311; R. G. W. Norrish and M. H. Searby, ibid., 1956, 237, 160.

disulphide accounts for Theilacker and Schmidt [5] having obtained the peroxide (3) from 1,2,3-triphenylisoindole (2) more cleanly in carbon disulphide than in dichloromethane [and our having obtained (17) instead in the latter solvent]. After hydrogen atom abstraction from dichloromethane (step 3 in Scheme 2), the ensuing dehydration to give the imines (14)—(17) is entirely expected by analogy with the behaviour of amine adducts of carbonyl compounds. Alternatively a diradical (22), arising *via* the peroxide or independently of it, could be the immediate precursor of the imines.

(22)

(23) R[1] = Me, R[2] = COPh
(24) R[1] = H, R[2] = COPh
(25) R[1] = H, R[2] = CO_2H
(26) R[1] = H, R[2] = Br
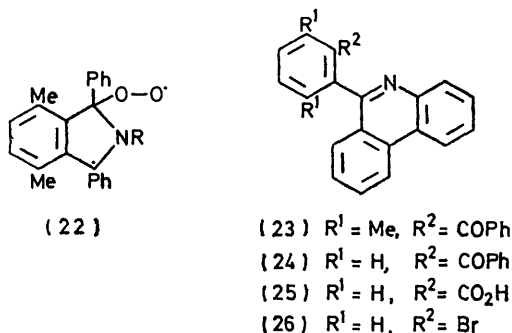
More prolonged irradiation of the isoindole (9) with bubbling oxygen in dichloromethane afforded a second product, m.p. 208—211°, formulated as the phenanthridine derivative (23). The i.r. and mass spectra of this compound show the presence of a benzoyl group, and the n.m.r. and mass spectra and elemental analysis confirm that its molecular formula differs from that of (9) only by two hydrogen atoms. The formation of (23) has a precedent in the photochemical cyclisation of benzophenone anil (18) to 6-phenylphenanthridine in the presence of oxygen or iodine as oxidant.[11]

Our second photoproduct from autoxidation of 1,2,3-triphenylisoindole (2) is then, by analogy, the phenanthridine (24). For this product an alternative formulation as 7-benzoyl-6-phenylphenanthridine is a possibility, if the cyclisation of the intermediate anil (17) had taken a different course. However, the correctness of structure (24) was established by comparison with a sample prepared independently by the reaction of phenyl-lithium with 2-(6-phenanthridyl)-benzoic acid (25). We also investigated another approach, requiring the reaction of a Grignard compound from 6-o-bromophenylphenanthridine (26) with benzoyl chloride, but this could not be realised.

EXPERIMENTAL

I.r. spectra of solids were recorded for Nujol mulls. [1]H N.m.r. spectra were measured at 60 MHz for solutions in deuteriochloroform with tetramethylsilane as internal standard. Low resolution mass spectra were recorded with an A.E.I. MS 12 instrument operating at 70 eV, with a direct insertion probe and with facility for rapid scanning of g.l.c. peaks. High resolution mass spectra were ob-

tained through the Physico-Chemical Measurements Unit, Aldermaston. G.l.c. analyses were performed on a column (1·6 m × 4 mm) containing silicone gum rubber SE 30 as stationary phase. Light petroleum was the fraction b.p. 60—80°. For photochemical experiments a water-cooled Hanovia 100 W medium-pressure mercury arc lamp in a Pyrex jacket was immersed in the solution through which oxygen or nitrogen could be bubbled.

Preparation of the isoindoles (6)—(9) has been described previously.[8,12] Treatment of the isoindole (6) with sodium nitrite in acetic acid gave 2,3-dibenzoyl-*p*-xylene (5), m.p. 141—142° (lit.,[8] 143°) [2,4-*dinitrophenylhydrazone*, orange needles, m.p. 205—206° (from ethanol) (Found: C, 67·8; H, 4·5; N, 11·4. $C_{28}H_{25}N_4O_5$ requires C, 68·0; H, 4·5; N, 11·3%)].

Autoxidation of 4,7-*Dimethyl*-1,3-*diphenylisoindole* (6).— A solution of the isoindole (6) (1·0 g) in light petroleum was heated under reflux for 2 h. After cooling, 63% of the starting material, m.p. and mixed m.p. 184—185°, was recovered, and no autoxidation product was detected.

A solution of the isoindole (6) (0·5 g) in dry tetrahydrofuran (50 ml) was heated under reflux with passage of oxygen during 48 h. Evaporation left a yellow oil, which slowly crystallised in the refrigerator. Recrystallisation from carbon disulphide and pentane afforded 1-*hydroperoxy*-4,7-*dimethyl*-1,3-*diphenyl*-1H-*isoindole* (10) (50 mg), m.p. 159—161° (decomp.), $\nu_{max.}$ *ca.* 3020br cm^{-1} (hydrogen bonded O—H $\cdots$ N), τ 2·41 and 2·81 (each 5H, s, ArH), 2·98 (2H, s, ArH), and 7·91 (6H, s, CH_3), m/e 329 (M^+, 38%), 313 (19), and 312 (M — OH, 100). When the hydroperoxide (10) was kept at ambient temperature for several days, it changed spontaneously into 1-*hydroxy*-4,7-*dimethyl*-1,3-*diphenyl*-1H-*isoindole* (11), m.p. 217—218° (decomp.) (Found: C, 84·1; H, 6·1; N, 4·6%; M^+, 313·1470. $C_{22}H_{19}NO$ requires C, 84·3; H, 6·1; N, 4·5%; M, 313·1467), τ [(CD_3)_2SO] 1·75 (OH, exchangeable in D_2O), 2·33, 2·50, and 2·64 (ArH), and 7·89 and 7·94 (CH_3) (spectrum poorly resolved).

The hydroperoxide (10) liberated iodine from acidified potassium iodide solution. A sample (180 mg) in tetrahydrofuran (5 ml) was added to sodium sulphite (3 g) in water (15 ml). This mixture was stirred for 12 h, and then extracted with ether. The extract was dried (MgSO_4) and evaporated to give the 1-hydroxy-1H-isoindole (11) (45 mg, 26%), m.p. and mixed m.p. 217—218° (decomp.).

Another sample of the crude autoxidation product from the isoindole (6) (0·5 g) was shaken with 2M-hydrochloric acid, and the mixture was extracted with ether. The residue from evaporation of the extract was chromatographed on alumina (Laporte type H), from which light petroleum–benzene eluted 2,3-dibenzoyl-*p*-xylene (5) (50 mg, 10%), m.p. and mixed m.p. 141—142°.

Autoxidation of 2,4,7-*Trimethyl*-1,3-*diphenylisoindole* (7). —A solution of the isoindole (7) (0·5 g) in dry tetrahydrofuran (50 ml) was heated under reflux with oxygen bubbling through for 43 h. Evaporation gave a yellow oil; this failed to crystallise, but g.l.c. analysis indicated the predominance (>95%) of one volatile component, identified as 3,6-*dimethyl*-2-(α-*methyliminobenzyl*)*benzophenone* (14) (Found: M^+, 327·1620. $C_{23}H_{21}NO$ requires M, 327·1623), $\nu_{max.}$ 1775, 1720, 1665, 1625, 1600, 1455, 1320, 1280br, 1175br, 1045, 995, 825, 735, and 705 cm^{-1}, τ 2·1—3·0 (10H,

[11] F. B. Mallory and C. S. Wood, *Tetrahedron Letters*, 1965, 2643.

[12] L. J. Kricka and J. M. Vernon, *J.C.S. Perkin I*, 1972, 904.

m, ArH), 3·36br (2H, ArH), 6·91 (3H, s, NCH$_3$), and 7·89 (6H, s, ArCH$_3$), m/e 327 (M^+, 15%), 298 (10), 251 (15), 250 (M − Ph, 100), 118 (PhC$\overset{+}{\equiv}$NMe, 12), 105 (7), and 77 (22).

The crude autoxidation product from another sample of the isoindole (7) in tetrahydrofuran was left for several days with added magnesium sulphate. Evaporation afforded the diketone (5) [76% based on the isoindole (7)], m.p. 140—141°, identical with an authentic sample (mixed m.p. and i.r. spectrum). Attempted distillation (b.p. 202—205° at 1·5 mmHg) of the crude imine (14) also resulted in extensive decomposition to the diketone (5).

Autoxidation of 2-Benzyl-4,7-dimethyl-1,3-diphenylisoindole (8).—The isoindole (8) in dry tetrahydrofuran was oxygenated under reflux as above. After 72 h the solvent was removed leaving a yellow oil, which was shown by g.l.c. analysis to consist mostly (>95%) of a single volatile component. The identification of the N-*benzylimine* (15) followed from the g.l.c.–mass spectrometry and other spectroscopic evidence (Found: M^+ − 1, 402·1858. C$_{29}$H$_{25}$NO requires M − 1, 402·1858; the molecular ion peak is broadened by interference from the [^{13}C$_1$]-component of the M^+ − 1 species. For this reason the accurate m/e ratio was determined instead for the more abundant M^+ − 1 peak); $\nu_{max.}$ 1665, 1625, 1600, 1460, 1280br, and 710 cm^{-1}, τ (CCl$_4$) 2·3—3·1 (17H, m, ArH), 5·50 and 5·88 (each 1H, d, J 17 Hz, N·CH$_2$Ph), and 7·85 and 7·96 (each 3H, s, CH$_3$), m/e 403 (M^+, 1%), 402 (2), 312 (25), 299 (25), 298 (100), 105 (68), 91 (64), 77 (85), with other significant peaks at m/e 315, 314, 313, 237, 235, 166, and 165 due to contamination with the diketone (5).

The crude autoxidation product was refluxed with *ca.* 0·5M-hydrochloric acid (aqueous ethanolic). The mixture was evaporated and the residue was recrystallised to give the diketone (5) [30% based on the isoindole (8)], m.p. and mixed m.p. 140—142°.

Autoxidation of 4,7-Dimethyl-1,2,3-triphenylisoindole (9). —The isoindole (9) (0·2 g) in dichloromethane (120 ml) was irradiated while dry oxygen was bubbled through the solution for 15 min. The solvent was evaporated off and the residue was chromatographed on silica (elution with benzene) to give the *monoanil* (16) of 2,3-dibenzoyl-*p*-xylene (5) (0·11 g, 53%), m.p. 141—142° (from benzene–light petroleum); m.p. depressed (111—128°) on admixture with compound (5) (Found: C, 86·3; H, 6·05; N, 3·7. C$_{28}$H$_{23}$NO requires C, 86·3; H, 5·95; N, 3·6%), $\nu_{max.}$ 1660, 1620, 1590, 1310, 1265, 1190, 1170, 1025, 960, 875, 845, 825, and 760 cm^{-1}, τ (CCl$_4$) 2·3—3·4 (17H, m, ArH) and 7·91 and 8·02 (each 3H, s, CH$_3$), m/e 390 (24%), 389 (M^+, 87), 388 (57), 312 (M − Ph, 100), 180 (PhC$\overset{+}{\equiv}$NPh, 28), 105 (23), and 77 (67), m^* 250 (389 ⟶ 312).

The anil (16) was hydrolysed in refluxing dilute aqueous ethanolic hydrochloric acid, as described above, to give the diketone (5) (85%), m.p. 139—141°, mixed m.p. with authentic material 139—142°.

U.v. irradiation of the isoindole (9) in dichloromethane under oxygen for longer periods gave mixtures of the anil (16) with the phenanthridine (23), which could be separated by column chromatography. For preparation of the second product, the isoindole (0·4 g) was irradiated for 70 min, the solvent was evaporated off, and the residue was chromatographed on silica. After elution with benzene (500 ml), further elution with benzene–ether (9 : 1 v/v) gave 3,6-*dimethyl-2-(6-phenanthridyl)benzophenone* (23)

(0·18 g, 42%), m.p. 208—211° (from benzene–light petroleum) (Found: C, 86·8; H, 5·5; N, 3·5. C$_{28}$H$_{21}$NO requires C, 86·8; H, 5·5; N, 3·6%), $\nu_{max.}$ 1660s, 1610w, 1590, 1580, 1280s, 865, 835s, 800w, 775s, 755, 735s, 725, and 710s cm^{-1}, τ 1·5—1·8 and 2·2—3·0 (15H, m, ArH) and 7·81 and 8·03 (each 3H, s, CH$_3$), m/e 388 (20%), 387 (M^+, 72), 386 (100), 358 (18), 310 (37), 308 (16), 280 (13), 278 (12), 266 (19), 193·5 (M^{2+}, 7), 105 (39), and 77 (36).

A solution of the isoindole (9) in dichloromethane in a Pyrex tube was thoroughly degassed by successive freeze-pump-thaw cycles, sealed, and irradiated externally with a Hanovia 400 W high-pressure mercury arc lamp for 1 h. The tube was opened, and the starting material (9) (93%) was recovered.

Autoxidation of 1,2,3-Triphenylisoindole (2).—A solution of the isoindole (2) in toluene was heated under reflux with passage of oxygen for 40 h, after which the starting material (2) was recovered; mixed m.p. 234° (lit.,[5] 234·5°).

After u.v. irradiation of a solution of the isoindole (2) in dry carbon disulphide with oxygen bubbling through, the peroxide (3) was isolated as described; [5] its m.p. was not sharp, but it liberated iodine from potassium iodide in aqueous acetic acid. This peroxide (3) (0·2 g) was heated in dichloromethane under reflux for 1 h; the solvent was evaporated off and the residue chromatographed on silica. Benzene eluted a crystalline product (0·05 g), m.p. 114—117°, the i.r. and mass spectra of which were identical with those of the monoanil (17) of o-dibenzoylbenzene (below). T.l.c. [silica; benzene–ether (9 : 1 v/v)] showed a single spot, R_F 0·60 [the same as that of the anil (17) prepared photochemically (below)]; no contamination with the diketone (4) was observed. Further elution of the column with benzene–ether (9 : 1 v/v) gave o-dibenzoylbenzene (4) (0·15 g), m.p. 146—148° (from benzene–hexane) (lit.,[5] 146—148°), identical with an authentic sample (i.r. and mass spectra and mixed m.p.).

The isoindole (2) (0·4 g) in dichloromethane (110 ml) with oxygen bubbling through was irradiated for 15 min. The solvent was evaporated off and the residue recrystallised (benzene–hexane) to give the *anil* (17) (0·23 g, 54%), m.p. 86—89° (Found: C, 86·65; H, 5·1; N, 3·8. C$_{26}$H$_{19}$NO requires C, 86·4; H, 5·3; N, 3·9%), $\nu_{max.}$ 1660s (C=O), 1620 (C=N), 1590, 1455, 1320, 1280br, 970, 955, 940, 800, 780, 770, 745, 720, and 710 cm^{-1}, m/e 361 (M^+, 26%), 332 (17), 284 (M − Ph, 44), 180 (PhC$\overset{+}{\equiv}$NPh, 17), 151 (19), 105 (18), 77 (100), and 51 (59), m^* 223 (361 ⟶ 284) and 56·5 (105 ⟶ 77).

The anil (17) was hydrolysed for 0·5 h in refluxing dilute aqueous ethanolic hydrochloric acid. The mixture was cooled and diluted with water; the diketone (4) (45%) was collected; m.p. and mixed m.p. 146—148°. The filtrate was made alkaline and extracted with ether; the ether layer was separated and the ether evaporated off leaving an oil smelling of aniline, which was diazotised and added to an alkaline solution of 2-naphthol, thereby giving a scarlet azo-dyestuff.

Irradiation of the isoindole (2) in dichloromethane with bubbling oxygen for 70 min gave 2-(6-phenanthridyl)benzophenone (24), which was isolated by chromatography on silica, elution with benzene–ether, and repeated recrystallisation (from carbon tetrachloride–hexane and then from chloroform–methanol); m.p. 158·5—161°, unchanged on admixture with the material with identical i.r. and mass spectra, the preparation of which is described below.

2-(6-Phenanthridyl)benzophenone (24).—N-*o*-Biphenylyl-

phthalimide, m.p. 166—168° (lit.,[13] 165—166°), reacted with zinc chloride at 275° as described by Koelsch [13] to give 2-(6-phenanthridyl)benzoic acid (25) only in very poor yield. An improved procedure was as follows. N-o-Biphenylylphthalimide (21·5 g) was added in portions to a stirred solution of anhydrous aluminium chloride (43·0 g) in nitrobenzene (40 ml) at 60° at such a rate so as to maintain this temperature without external heating. Hydrogen chloride was copiously evolved. After addition was complete, the mixture was stirred and heated at 150—160° for 30 min and then at 180—200° for 10 min. It was cooled and poured onto crushed ice with addition of concentrated hydrochloric acid (3 ml). After 1 h the organic layer was separated and diluted with light petroleum. The crude product thus precipitated was filtered off and washed with light petroleum; it was then dissolved in aqueous sodium carbonate (5% w/w). This solution was filtered and the filtrate was neutralised with dilute hydrochloric acid. The precipitated acid (25) was collected, washed, dried, and recrystallised (ethanol–ethyl acetate); m.p. 270—272° (lit.,[13] 268—270°) (yield 15·7 g, 73%). The m.p. was raised to 274—276° after a subsequent recrystallisation (from acetic acid).

A solution of phenyl-lithium [from lithium (0·4 g) and bromobenzene (3·4 g)] in dry ether, was filtered from unchanged lithium through glass wool and added dropwise to a stirred suspension of the acid (25) (1·3 g) in dry ether. The mixture was stirred overnight, and then refluxed for 1 h. Water was added, and the ether layer was separated, dried (MgSO₄), and evaporated. The residue afforded the *phenanthridine* (24) (1·0 g, 65%), m.p. 160—162° (from chloroform–methanol) (Found: C, 87·1; H, 5·0; N, 3·8. $C_{26}H_{17}NO$ requires C, 86·9; H, 4·8; N, 3·9%), $\nu_{max.}$ 1655s (C=O), 1610w (C=N), 1595, 1575, 1360, 1315, 1290, 1275, 1160, 970, 950, 935, 795, 780s, 770, 740, 730, and 710s cm⁻¹, *m/e* 359 (M^+, 5%), 283 (22), 282 (*M* − Ph, 100), 254 (11), 253 (15), 179·5 (M^{2+}, 3), 105 (3), and 77 (12), *m** 221·5 (359 —▶ 282) and 229 (282 —▶ 254). The same preparation with only 2 equiv. instead of an excess of phenyl-lithium gave a lower yield of the product (24), and some acid (25) was recovered.

6-(o-*Bromophenyl*)*phenanthridine* (26).—o-Bromobenzoyl chloride, prepared from o-bromobenzoic acid (4·02 g) with thionyl chloride, was dissolved in dry pyridine and added in one portion to o-aminobiphenyl (3·38 g) in pyridine.

The mixture was stirred for 2 h, then poured into water, and stirring was continued for 1 h. The precipitate was collected, washed with water, and recrystallised (ethanol–light petroleum) to give N-o-*biphenylyl-2-bromobenzamide* (5·0 g, 71%), m.p. 113—114·5° (Found: C, 64·6; H, 3·8; N, 4·1. $C_{19}H_{14}BrNO$ requires C, 64·8; H, 4·0; N, 4·0%), $\nu_{max.}$ 3250 (N–H) and 1650 (C=O) cm⁻¹, *m/e* 353/351 (M^+, 46/46%), 272 (*M* − Br, 11), 185/183 (o-BrC₆H₄CO⁺, 100/100), 167 (27), and 157/155 (BrC₆H₄⁺, 24/24), *m** 210br (353 and 351 —▶ 272), 133 (185 —▶ 157), 131 (183 —▶ 155), 97 (353 —▶ 185), and 95 (351 —▶ 183).

This amide (4·4 g) in phosphoric trichloride was heated under reflux for 5 h. Phosphoric trichloride was then distilled off under reduced pressure, and the residue was treated with aqueous sodium hydrogen carbonate (8%). The resulting gum solidified on trituration with acetone, but the solid was still impure. It was filtered off, redissolved in chloroform, and shaken repeatedly with aqueous sodium hydrogen carbonate and finally with water. The chloroform layer was separated, dried (MgSO₄), and evaporated to give 6-(o-*bromophenyl*)*phenanthridine* (26) (2·2 g, 53%), m.p. 157·5—159·5° (Found: C, 68·3; H, 3·8; N, 4·1. $C_{19}H_{12}BrN$ requires C, 68·3; H, 3·6; N, 4·2%), $\nu_{max.}$ 1610 (C=N), 1590w, 1575, 1530, 1490, 1330, 1300, 1235, 1160, 1140br, 1120, 1050, 1030, 970, 950, 870, 855, 790, 775s, 760s, and 730 cm⁻¹, *m/e* 335, 333 (M^+, 16/16%), 255 (20) and 254 (*M* − Br, 100), *m** 195 and 194 (335 and 333 —▶ 254, respectively).

The same product (26) was also obtained in a one-step procedure [14] as follows. o-Bromobenzoic acid (4·02 g), o-aminobiphenyl (3·38 g), and polyphosphoric acid (55 g) were mixed and heated at 180—200° for 45 min with occasional shaking. The mixture was cooled in ice, diluted with water, and filtered. The filtrate was neutralised with aqueous ammonia (d 0·88), and the resulting gum was stirred with water overnight. The crude solid so obtained was filtered off and purified as described above to afford the same phenanthridine (26) (2·3 g, 55%), m.p. and mixed m.p. 156·5—158·5°.

[13] C. F. Koelsch, *J. Amer. Chem. Soc.*, 1936, **58**, 1325.
[14] B. Staskun, *J. Org. Chem.*, 1964, **29**, 2856.