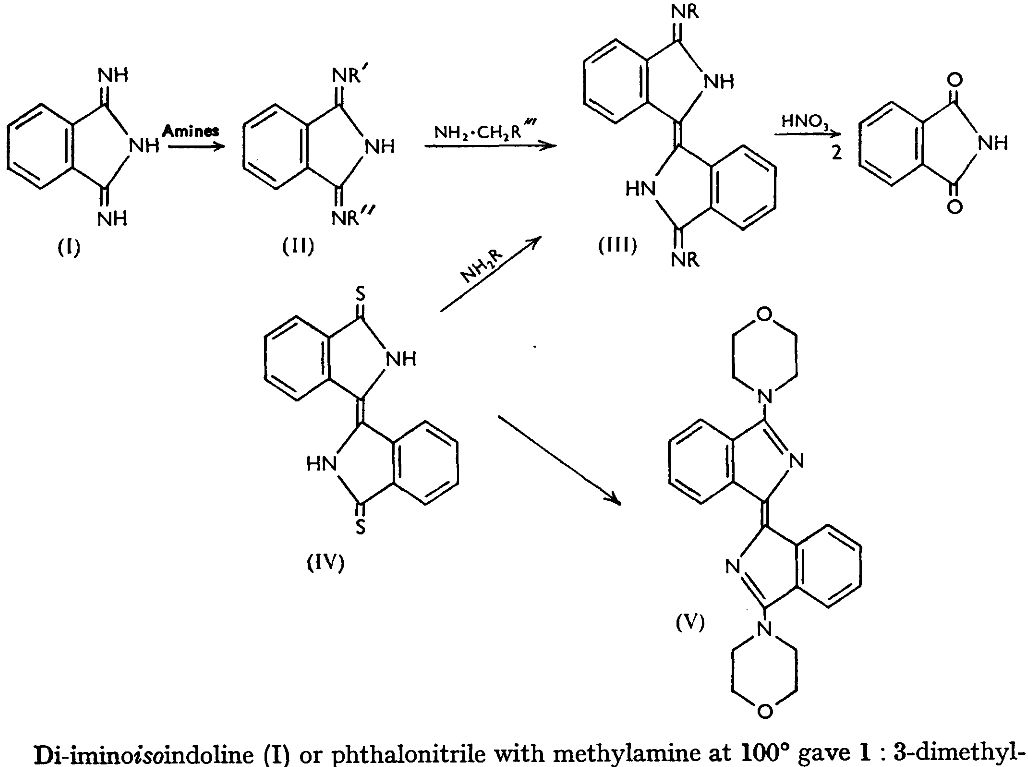
800. *Compounds containing Directly Linked Pyrrole Rings. Part II.* Dialkylimino*-β-iso*indigos.*

By J. A. ELVIDGE and J. H. GOLDEN.

1 : 3-Dimethyliminoisoindoline (II; R′ = R″ = Me) with methylamine at 200° affords dimethylimino-β-*iso*indigo † [di-(3-methylimino-1-*iso*indolinylidene)] (III; R = Me), which on oxidative hydrolysis gives 2 mols. of phthalimide. Dibutyl- and dibenzyl-imino-β-*iso*indigo (III; R = Bu and CH_2Ph) are obtained analogously: they can also be prepared from dithio-β-*iso*indigo (IV) with butylamine and benzylamine respectively. Condensation of morpholine with dithio-β-*iso*indigo gives a derivative with the fixed-bond structure (V). Light absorptions are given, and the fine structure of the new β-*iso*indigo derivatives is discussed.

Their formation from imidines and alkylamines evidently proceeds *via* a bimolecular reduction, the alkylamine, $R'''\cdot CH_2\cdot NH_2$, acting as the hydrogen donor.

TREATMENT of di-imino*iso*indoline (I) with primary amines under mild conditions yields substituted imino*iso*indolines (II).[1,2,3] We now find that under more vigorous conditions, β-*iso*indigo derivatives (III) are formed. This unexpected reaction (II) ⟶ (III) is a bimolecular reduction.



Di-imino*iso*indoline (I) or phthalonitrile with methylamine at 100° gave 1 : 3-dimethyliminoisoindoline[3] (II; R′ = R″ = Me). When this compound, $C_{10}H_{11}N_3$, was heated with methylamine at 200°, in an attempt to prepare a trimethyl derivative, a high-melting

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* Part I, *J.*, 1956, 244.

† Drew and Kelly (*J.*, 1941, 625, 630) called the compound (IV) "dithio-β-*iso*indigo."

[1] Elvidge and Linstead, *J.*, 1952, 5000.

[2] Clark, Elvidge, and Linstead, *J.*, 1953, 3593.

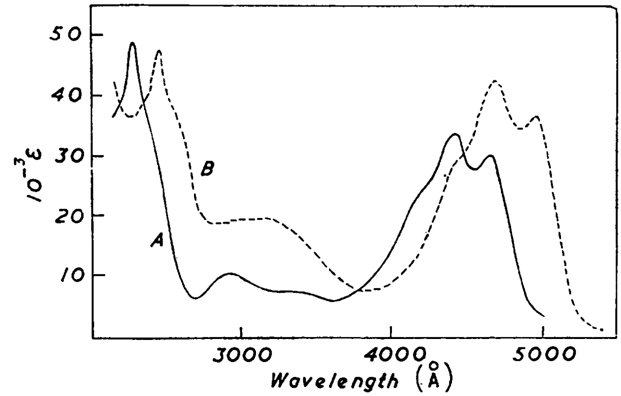
[3] Clark, Elvidge, and Golden, preceding paper.

orange product was obtained instead, whose analyses indicated a formula $C_9H_8N_2$. This was got in better yield from phthalonitrile and methylamine without the isolation of intermediate imidines.

The new product gave values for active hydrogen of approximately 0·5 and 1, by the Zerewitinoff and the lithium aluminium hydride method, respectively. The compound was practically unaffected by boiling dilute sodium hydroxide, hydrochloric acid, or sulphuric acid. However, boiling dilute nitric acid readily effected oxidative hydrolysis to phthalimide (in high yield) and methylamine, a result which indicated the presence of the intact *iso*indoline nucleus. The fragments $C_6H_4{<}\overset{C}{\underset{C}{}}{>}NH$ and NMe accounted for the empirical formula but could not provide a feasible structure or account for 0·5 atom of active hydrogen. Hence it was concluded that the orange compound must have a " double " molecule, $C_{18}H_{16}N_4$, *i.e.*, that it had the β-*iso*indigoid structure (III; R = Me). Support for this came first from a molecular-weight determination in acetone by a modification of the Barger method.[4]

Proof of the structure (III; R = Me) was achieved by a synthesis from dithio-β-*iso*-indigo (IV) and ethanolic methylamine. Drew and Kelly[5] had earlier prepared the diphenylimine (III; R = Ph) by this route. The light absorptions of these imines are similar (see Figure).

Light absorption of (*A*) *di-*(*3-methylimino-*1-iso*indolinylidene*) (*in dioxan*) *and* (*B*) *di-*(*3-phenylimino-*1-iso*indolinylidene*) (*in ethanol*).



Benzylamine and butylamine behaved similarly to methylamine when reacting with imidines at elevated temperatures. Thus heating 1 : 3-dibenzylimino*iso*indoline (II; R′ = R″ = CH_2Ph) with benzylamine in butanol, or di-imino*iso*indoline (I) with butylamine at 200°, afforded orange products, $C_8H_5N_2R$, where R = C_7H_7 or C_4H_9, respectively. These had similar general properties and light absorptions (see Table) to the methylamine product and were presumably the β-*iso*indigoid imines (III). Oxidative hydrolyses did not proceed cleanly, however, although the dibenzylimine gave some phthalimide, together with benzaldehyde, presumably from oxidation of the benzylimino-groups. Attempted conversion of the imines (III) into dithio-β-*iso*indigo (IV) failed. The structures (III; R = CH_2Ph and C_4H_9) were made certain, however, by the syntheses (IV) ⟶ (III), from dithio-β-*iso*indigo with benzylamine and butylamine. These reactions, like that with methylamine, proceeded with evolution of hydrogen sulphide and were evidently straightforward displacements of the sulphur groups in dithio-β-*iso*indigo by the alkylamine residues.

The structures (III) for the new orange products were thus certain apart from questions of fine structure, *viz.*, (*a*) geometrical isomerism, (*b*) tautomerism, and (*c*) mesomerism.

(*a*) Scale models, constructed on covalent atomic radii, indicated that the preferred

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[4] Niederl, Kasanof, Kisch, and Subba Rao, *Mikrochemie*, 1949, **34**, 132.

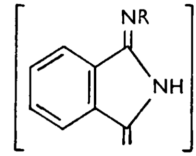
[5] Drew and Kelly, *J.*, 1941, 630.

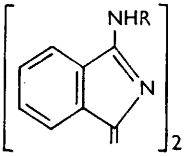
orientation of these molecules about the central double bond is *trans*. In the *cis*-form there would be hindrance between the benzene rings.

In agreement, the dialkylimino-β-*iso*indigos (III; R = Me, Bu, and CH_2Ph) were found not to form complexes with metals. Dithio-β-*iso*indigo does so,[6] but it seems that its metal derivatives may be mercaptides, rather than nitrogen-co-ordination complexes of the *cis*-form as suggested by Drew and Kelly.[6]

(*b*) The molecules (III) are potentially tautomeric: two of the possible forms are *A* and *B*, and a third is $\frac{1}{2}A + \frac{1}{2}B$. In order to gain information on the preferred positions of the active hydrogens, we prepared the derivative (V), which has a fixed bond structure, by condensing dithio-β-*iso*indigo with morpholine. Derivative (V) shows a principal maximum in the visible at 4800 Å with an inflexion at 4960 Å (see Table). The compounds (III; R = alkyl) have two main maxima in the visible at shorter wavelengths, in the regions 4400—4500 and 4660—4720 Å respectively. The phenyl derivative (III; R = Ph) has maxima at 4680 and 4950 Å. By analogy with the 3-(substituted imino)-1-oxo*iso*indolines,[2, 3] it seems likely that for the alkyl-substituted di-imino-β-*iso*indigos (III; R = Me, Bu, and CH_2Ph) the position of tautomeric equilibrium (in dioxan) is towards the di-1-*iso*indolinylidene form *A*, whereas for the phenyl-substituted compound (in the solvents named in the Table) it is towards the tautomeric form *B*.

(A)





(B)

(*c*) The light absorptions of the new β-*iso*indigo derivatives (see Table) are compatible with the bond structures assigned: there is no absorption at unexpectedly long wavelengths. Hence the compounds are evidently not appreciably mesomeric, and in that respect they differ markedly from the dipyrrolidinylidene described by Elvidge, Fitt, and Linstead.[7] Indeed most of the electronic isomers of the structures (III) would carry negative charges upon nitrogen, so that mesomerism in these molecules would not be favoured.

Light absorptions.

Compound	Solvent	$\lambda_{max.}$ (Å)	ε	Compound	Solvent	$\lambda_{max.}$ (Å)	ε
(III) R = Me ...	Dioxan	2280	49,400	(III) R = Ph ...	Benzene	3150	11,600
		2930	10,900			4640	33,100
		4410	34,200			4940	31,000
		4660	30,300				
					Ethanol	2460	47,500
R = Bu ...	,,	2280	44,700			3040 3170	19,500
		2940	8,200				
		3330	6,100			4680	42,500
		4500 4720	32,400			4950	36,500
				(V)	,,	2440	32,000
R = CH_2Ph	,,	2270	74,800			2980 3050	6,000
		2950	13,600				
		4480	37,400			4800	28,400
		4700	34,800			4960 *	24,800

All the solutions showed an intense green fluorescence under ultraviolet light. * Inflexion.

Evidence was sought for the existence of a more highly conjugated dehydro-form of the β-*iso*indigo derivatives, *viz.*, (VI). However, attempted dehydrogenation of the β-*iso*indigoid system (III) by means of lead dioxide, as with indigoids,[8] was unsuccessful, and attempts with quinones [9] were inconclusive.

Formation of the β-iso*Indigoids*.—The reaction (II) ⟶ (III) could not be achieved with

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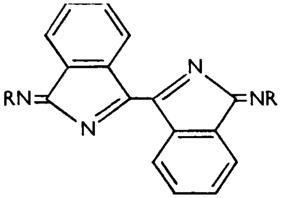
[6] Drew and Kelly, *J*, 1941, 625.
[7] Elvidge, Fitt, and Linstead, *J.*, 1956, 244.
[8] Madelung, *Annalen*, 1914, **405**, 58; Kalb, *Ber.*, 1909, **42**, 3642.
[9] Braude, Brook, and Linstead, *J.*, 1954, 3569; Eisner and Linstead, *J.*, 1955, 3749.

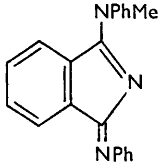
ammonia or aniline, *i.e.*, it could not be extended to the cases where $R = R' = R'' = H$ and $R = R' = R'' = Ph$. Thus heating di-imino*iso*indoline (I) with ammonia at 200° gave only a trace of phthalocyanine, and most of the imidine (I) was recovered. Nothing identifiable was obtained after heating of 1 : 3-diphenylimino*iso*indoline (II; $R' = R'' = Ph$) with aniline in ethyl carbitol (ethylene glycol ethyl ether) for 24 hr. Heating at 250° in ethanol for 72 hr. produced some complex changes; phthalamide and 1-oxo-3-phenylimino*iso*indoline were isolated and an accompanying trace of pigment was found to be a mixture of phthalocyanine with tetrabenzotriazaporphin. No other product was identified.

On the other hand, when 1 : 3-diphenylimino*iso*indoline (II; $R' = R'' = Ph$), or better 1-imino-3-phenylimino*iso*indoline (II; $R' = H$, $R'' = Ph$), was heated in ethyl carbitol with benzylamine, the dibenzylimino-β-*iso*indigo (III; $R = CH_2Ph$) was produced. This β-*iso*indigo derivative was also obtained, by means of benzylamine in boiling butanol, from 1 : 3-dimethylimino*iso*indoline (II; $R' = R'' = Me$) and, interestingly, from 3-*N*-methylanilino-1-phenylimino*iso*indolenine (VII)[2] though in poor yield, but not apparently from 2-methyl-1 : 3-diphenylimino*iso*indoline (VIII).[3] The reaction liquors from the successful experiments contained benzaldehyde.

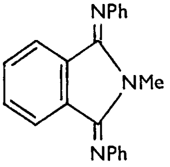
The displacement of a substituted imino-group by another in reactions of imidines with amines is known[1,3] and warrants no special comment here. Of particular significance, though, was the rôle of benzylamine in coupling the pyrrolic nuclei, itself apparently giving rise to benzaldehyde. In the favourable case of 1 : 3-dibenzylimino*iso*indoline (II; $R' = R'' = CH_2Ph$) already mentioned, an excess of benzylamine was required for the production of the β-*iso*indigo (III; $R = CH_2Ph$) in reasonable yield; no β-*iso*indigo derivative was formed from the *iso*indoline (II; $R' = R'' = CH_2Ph$) merely by boiling it in butanol with pyridine, triethylamine, a *trace* of benzylamine, or with *cyclo*hexene alone or in the presence of palladium.



(VI)



(VII)



(VIII)

It seemed reasonable to suppose therefore that the formation of the β-*iso*indigo derivatives (III) from alkylimino*iso*indolines (II) (or phthalonitrile) and alkylamines involved a bimolecular reduction, the alkylamine being the specific hydrogen donor. When 1-imino-3-phenylimino*iso*indoline (II; $R' = H$, $R'' = Ph$) and benzylamine were boiled together in purified *tert.*-amyl alcohol, the dibenzylimino-β-*iso*indigo (III; $R = CH_2Ph$) was formed in 48% yield. Treatment of the filtrate with dinitrophenylhydrazine reagent afforded the derivative of benzaldehyde to the extent of almost 2 molecular proportions, calculated on the imidine derivative consumed. In the absence of the imidine (II; $R' = H$, $R'' = Ph$) no carbonyl compound was formed. Thus the benzylamine is indeed the bimolecular reducing agent in this reaction, functioning by the process $NH_2{\cdot}CH_2Ph \longrightarrow 2H + NH{:}CHPh\ (\xrightarrow{H_2O} Ph{\cdot}CHO)$ at the demand of the imidine. Methylamine and butylamine can fill a similar rôle but not, of course, ammonia or aniline. The various experimental results indicate that the overall reductive coupling process is $2(II) + 4H \longrightarrow (III) + 2NH_2R$. This type of reaction is being studied.

EXPERIMENTAL

Analyses were by Mr. F. H. Oliver and his staff of the microanalytical laboratory and the ultraviolet measurements by Mrs. A. I. Boston of the spectrographic laboratory of this Department.

*Di-(3-methylimino-*1-iso*indolinylidene)* (*Dimethylimino-*β-iso*indigo*) (III; $R = Me$).—(a) *Preparation.* (i) 1 : 3-Dimethylimino*iso*indoline[3] (II; $R' = R'' = Me$) (3 g.) was heated with dry methylamine (5 c.c.) and ethanol (15 c.c.) at 200° for 24 hr. After it had cooled, the solution deposited orange crystals (20 mg.), m. p. 308° (decomp.). From dioxan, *di-(3-methylimino-*1-iso-*indolinylidene)* formed orange plates, m. p. 317—318° (decomp.) [Found: C, 75·3; H, 5·9; active H, (Zerewitinoff), 0·31, ($LiAlH_4$ in Bu_2O) 0·88, 0·91; N, 19·6%; *M* (Barger,[4] in acetone), 236, 258. $C_{18}H_{16}N_4$ requires C, 75·0; H, 5·6; 2 active H, 0·70; N, 19·4%; *M*, 288]. Concentration of the reaction mother-liquors under reduced pressure afforded 1 : 3-dimethylimino-*iso*indoline (2·7 g.), m. p. and mixed m. p. 169°.

(ii) Phthalonitrile (5 g.) was heated with methylamine (12 c.c.) and ethanol (15 c.c.) at 100° for 24 hr. and then at 200° for 20 hr. The solution was filtered hot, and the orange product (1·7 g., 28%), m. p. *ca.* 312° (decomp.), was washed with methanol and recrystallised from dioxan, to afford the dimethylimino-β-*iso*indigo as orange plates, m. p. and mixed m. p. 317—318° (decomp.). The reaction liquors were treated with charcoal and concentrated under reduced pressure. Addition of benzene to the residual syrup caused 1 : 3-dimethylimino*iso*indoline to crystallise (2 g.; m. p. and mixed m. p. 165°).

(b) *Oxidative hydrolysis.* The dimethylimino-β-*iso*indigo (189 mg.) was warmed on the steam-bath with 2N-nitric acid (6 c.c.) for 2—3 min. The clear solution was chilled in ice, and after 15 min. the precipitated phthalimide was collected, washed, and dried (186 mg., 94%; m. p. and mixed m. p. 234°). The filtrate was evaporated to dryness and the residue treated with alkali: methylamine was recognised by smell.

*Di-(3-phenylimino-*1-iso*indolinylidene)* (III; R = Ph).—This was prepared by Drew and Kelly's method [6] from dithio-β-*iso*indigo.

*Di-(3-butylimino-*1-iso*indolinylidene)* (III; R = Bu).—(i) 1 : 3-Di-imino*iso*indoline [1] (I) (5 g.) was converted with *n*-butylamine (10 c.c., redistilled) in ethanol (15 c.c.) at 100° into the 1 : 3-dibutylimine (II; R = R′ = Bu) (cf. ref. 2), and the solution was then kept at 200° for 24 hr. The cooled solution deposited orange-red crystals (1·5 g., 24%), m. p. 239° (decomp.). From dioxan (charcoal), *di-(3-butylimino-*1-iso*indolinylidene)* formed orange prisms, m. p. 244° (decomp.) [Found: C, 77·4; H, 7·7; active H ($LiAlH_4$), 0·63, 0·58; N, 15·2. $C_{24}H_{28}N_4$ requires C, 77·4; H, 7·6; 2 active H, 0·54; N, 15·1%].

(ii) Heating of di-imino*iso*indoline (5 g.) with butylamine (10 c.c.) in butanol (15 c.c.) for 72 hr. afforded the dibutylimino-β-*iso*indigo (1·5%) and (from the mother-liquors, by evaporation) 1 : 3-dibutylimino*iso*indoline (58%), identified by m. p.s and mixed m. p.s.

(iii) Dithio-β-*iso*indigo [5] (IV) (95 mg.) was heated under reflux with butylamine (4 c.c.) for 1 hr. The solution was evaporated to 1 c.c., diluted with ether (100 c.c.), and kept overnight at 0°. Orange crystals of dibutylimino-β-*iso*indigo (58 mg., 48%), m. p. and mixed m. p. 242° (decomp.), separated.

*Di-(3-benzylimino-*1-iso*indolinylidene)* (III; R = CH_2Ph).—(a) *Preparation.* (i) 1 : 3-Dibenzylimino*iso*indoline [3] (II; R′ = R″ = CH_2Ph) (300 mg.), butanol (5 c.c.), and benzylamine (2 c.c.) were heated together under reflux for 24 hr. When the solution had been concentrated under reduced pressure to 3 c.c. and cooled, orange crystals (71·5 mg., 35%), m. p. 299° (decomp.), separated. Recrystallisation of the product from dioxan afforded orange-red felted needles of di-(3-benzylimino-1-*iso*indolinylidene), m. p. 302° (decomp.) with darkening from *ca.* 280° (Found: C, 81·9; H, 5·7; N, 12·8. $C_{30}H_{24}N_4$ requires C, 81·8; H, 5·5; N, 12·7%).

(ii) Di-imino*iso*indoline [1] (I) (8 g.), benzylamine (16 c.c.), and butanol (50 c.c.) were heated together under reflux for 56 hr. Ammonia was rapidly evolved initially and the solution soon became dark red. From the cold solution, the dibenzylimino-β-*iso*indigo separated as orange crystals (2 g., 17%), m. p. 284° (decomp.), and m. p. 302° (decomp.) after recrystallisation from dioxan.

(iii) Dithio-β-*iso*indigo [5] (IV) (114 mg.) and benzylamine (4 c.c.) were heated together under reflux. There was a slow evolution of hydrogen sulphide. After 1 hr., the brown solution was cooled and poured into ether (40 c.c.), and the orange crystalline precipitate (65 mg.) was subsequently collected. Addition of more ether (40 c.c.) and cooling to 0° overnight afforded a second crop (45 mg.): the total yield was 65%, and the m. p. and mixed m. p. 299° (decomp.).

(b) *Oxidative hydrolysis.* Warming the dibenzylimino-β-*iso*indigo (319 mg.) with 2N-nitric acid (10 c.c.) on the steam-bath for 35 min. afforded a pale orange solution containing suspended solid: the mixture smelled strongly of benzaldehyde. The mixture was cooled in ice and filtered. Extraction of the solid (286 mg.) with hot water yielded needles of phthalimide, m. p. and mixed m. p. 232°.

Attempted Thiohydrolyses.—The dibenzylimino-β-*iso*indigo (214 mg.) was boiled in dioxan (15 c.c.) with aqueous ammonium polysulphide (5 c.c.; 16%) for 18 hr. After cooling of the solution, the β-*iso*indigo derivative was recovered (209 mg.), identified by m. p. and mixed m. p.

The dimethylimino-β-*iso*indigo was likewise unaffected by similar treatment. The solution did not develop a purple colour.

Attempted Metallation.—(i) There was no change in visible light absorption when solutions of the imino-β-*iso*indigos in pyridine and dimethylformamide were mixed with nickel and copper acetates in these solvents.

(ii) The dibenzylimino-β-*iso*indigo was recovered after being heated under reflux in pyridine with anhydrous cobalt acetate for 1 hr.

*Di-(3-morpholino-*1-iso*indoleninylidene)* (V).—(a) *Preparation.* Dithio-β-*iso*indigo (IV) (0·4 g.) and morpholine (5 c.c.) were heated together under reflux for 2·5 hr. Hydrogen sulphide was evolved. As the solution cooled, it deposited orange crystals (0·27 g.), m. p. 314—315° (decomp.). From dioxan *di-(3-morpholino-*1-iso*indoleninylidene)* formed orange needles, m. p. 319—320° (decomp.) (Found: C, 72·1; H, 6·2; N, 14·3. $C_{24}H_{24}O_2N_4$ requires C, 72·0; H, 6·0; N, 14·0%).

(b) *Oxidative hydrolysis* [with M. E. Baguley]. The preceding derivative (270 mg.) was heated with 2N-nitric acid at 100° for 5 min. The mixture was then cooled in ice. The solid (190 mg., 1·79 mols.) was identified as phthalic acid (positive fluorescein reaction) by mixed m. p. 192—195°.

Attempted Dehydrogenation[8] *of Dibenzylimino-*β-iso*indigo* (III; R = CH_2Ph).—The β-*iso*-indigo (0·34 g.), lead dioxide (2·8 g.), and anhydrous calcium chloride (2 g.) were boiled together in benzene (50 c.c.) for 5 hr. Evaporation of the filtrate to dryness afforded a reddish solid (215 mg.), contaminated with traces of lead compounds. The solid did not depress the m. p. of dibenzylimino-β-*iso*indigo. In dioxan solution the product and the starting material had closely similar light absorption characteristics. Addition of acetic acid to a second reaction mixture caused destruction of the β-*iso*indigoid.

*Attempted Reaction of Di-imino*iso*indoline* (I) *with Ammonia under Vigorous Conditions.*—Phthalonitrile (3 g.) was converted with ammonia (7 c.c. of liquid) in dry ethanol (20 c.c.) at 100° into di-imino*iso*indoline (cf. ref. 1), and the solution was then kept at 200° for 24 hr. Filtration of the solution from phthalocyanine (40 mg.; identified spectroscopically) and concentration of the filtrate under reduced pressure afforded 1 : 3-di-imino*iso*indoline (3·3 g., 97%), m. p. and mixed m. p. 195° (decomp.).

*Action of Aniline on Phenylimino*iso*indolines under Vigorous Conditions.*—(i) Phthalonitrile (6 g.) was treated with aniline (15 c.c.) in ethanol (15 c.c.) at 100° for 24 hr. as for conversion into 1 : 3-diphenylimino*iso*indoline (II; R′ = R″ = Ph) (cf. ref. 2), and the solution was then heated at 200—250° for 72 hr. A greenish solid *A* (0·51 g.) was filtered from the ammoniacal liquor which was then concentrated under reduced pressure to a syrup. Treatment of the latter with ether afforded a yellowish-brown solid *B* (87 mg.), m. p. 224°. The filtrate was evaporated, the residue taken up in methanol, and the solution treated with charcoal and evaporated. Treatment of the sticky solid residue with ether (100 c.c.) then gave a yellow powder *C* (2·9 g.), m. p. 157° (decomp.).

Solid *A* was warmed with methanol (200 c.c.), and the solution, filtered from insoluble pigment (28 mg.), shown spectroscopically to be a mixture of phthalocyanine and tetrabenzotriazaporphin[10] ($\lambda_{\text{max.}}$ 693 > 665, 650 > 595 ≫ 634, 619). Evaporation and cooling of the filtrate yielded a crystalline solid (352 mg.), m. p. 223°, identical with *B*.

Solid *B* was recrystallised from methanol–butanol, affording phthalamide, m. p. and mixed m. p. 224° (Found: N, 17·2. Calc. for $C_8H_8O_2N_2$: N, 17·1%).

Solid *C* was crystallised extractively from light petroleum (b. p. 60—80°) and then from ethanol ordinarily. 1-Oxo-3-phenylimino*iso*indoline was obtained, having m. p. 168° undepressed by authentic material.[1]

(ii) 1-Imino-3-phenylimino*iso*indoline[2] (II; R′ = H, R″ = Ph) (0·5 g.) and aniline (3 c.c.) in boiling ethyl carbitol (3 c.c.) for 24 hr. gave only 1 : 3-diphenylimino*iso*indoline (294 mg.), m. p. and mixed m. p. 129—130°.

(iii) From a similar experiment with 1 : 3-diphenylimino*iso*indoline nothing identifiable was obtained.

Related Experiments.—No dibenzylimino-β-*iso*indigo was obtained by boiling 1 : 3-dibenzyliminoisoindoline (0·3 g.) in butanol (5 c.c.) for 24 hr. alone, or with a trace of benzylamine (5 mg.), with triethylamine (2 c.c.), with pyridine (2 c.c.), with *cyclo*hexene, or with *cyclo*hexene (5 c.c.) and 5% palladium–charcoal (10 mg.).

*Action of Benzylamine on Phenylimino*iso*indolines.*—(i) 1 : 3-Diphenylimino*iso*indoline (II; R′ = R″ = Ph) (0·5 g.) and benzylamine (3 c.c.) were boiled in ethyl carbitol (3 c.c.) for 24 hr.

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[10] Barrett, Linstead, and Tuey, *J.*, 1939, 1809.

The solution was evaporated to 2 c.c. under reduced pressure, and benzene (5 c.c.) was added. During 3 weeks, orange crystals of dibenzylimino-β-*iso*indigo (III; $R = CH_2Ph$) (18 mg.) separated; it had m. p. 285° (decomp.), raised after a crystallisation from dioxan to 301° (decomp.) undepressed by authentic material.

(ii) 1-Imino-3-phenyliminoisoindoline (0·5 g.) and benzylamine (3 c.c.) in boiling ethyl carbitol (3 c.c.) similarly gave dibenzylimino-β-*iso*indigo (53 mg.), m. p. 286° (decomp.), which after crystallisation from dioxan had m. p. and mixed m. p. 301° (decomp.).

(iii) 1 : 3-Dimethylimino*iso*indoline (1·73 g.) was heated under reflux with benzylamine (2·14 g.) in butanol (5 c.c.) for 48 hr. The solution, which smelled of benzaldehyde, was evaporated to 3 c.c. and diluted with ether (40 c.c.), and 2 weeks later the yellow crystals were collected [32 mg.; m. p. 290° (decomp.)]. After being recrystallised from dioxan, the product had m. p. 295° (decomp.) undepressed by dibenzylimino-β-*iso*indigo but depressed by dimethylimino-β-*iso*indigo.

(iv) 3-*N*-Methylanilino-1-phenylimino*iso*indolenine[2] (VII) (0·5 g.), butanol (5 c.c.), and benzylamine (3 c.c.) were boiled together for 17 hr., and the solution was then evaporated under reduced pressure to a small volume, and ether was added. After 24 hr., orange crystals (71 mg.) had separated; these had m. p. 299° (with some previous softening) undepressed by dibenzylimino-β-*iso*indigo (III; $R = CH_2Ph$). The filtrate was diluted with chloroform and washed with aqueous hydrochloric acid. The chloroform was evaporated and the residue extracted with ether several times. Evaporation of the ether and treatment of the oily residue in ethanol with an ethanolic sulphuric acid solution of 2 : 4-dinitrophenylhydrazine at once afforded the derivative of benzaldehyde (292 mg., m. p. and mixed m. p. 232—233°).

(v) A solution of 1-imino-3-phenylimino*iso*indoline (500 mg.) in *tert.*-amyl alcohol (3 c.c.; previously refluxed with sodium and distilled) was boiled with benzylamine (3 c.c.) for 48 hr. and then kept at room temperature for 48 hr. The orange crystalline product (242 mg., 48%) had m. p. 299° (decomp.) not depressed by dibenzylimino-β-*iso*indigo. Treatment of the filtrate with an excess of ethanolic 2 : 4-dinitrophenylhydrazine sulphate afforded benzaldehyde 2 : 4-dinitrophenylhydrazone (621 mg., 96%), m. p. and mixed m. p. 237°.

(vi) No benzaldehyde derivative was obtained from a duplicate experiment in which the 1-imino-3-phenylimino*iso*indoline had been omitted.

We gratefully acknowledge a maintenance award (to J. H. G.) from the Department of Scientific and Industrial Research.

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[*Received, April 3rd*, 1956.]