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The Reactions of Phenols with Phthalodinitrile and 3-Amino-1*H*-isoindoles

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Phenols react with phthalodinitrile, alone or catalysed by hydrogen chloride to give 2-amino-1,1-di(hydroxyaryl)-1*H*-isoindoles. The hydrogen chloride-catalysed reaction of *para*-cresol is anomalous. These amino-1*H*-isoindoles react further with phenols with the liberation of ammonia and the formation of 1,3,3-tri(hydroxyaryl)-1*H*-isoindoles and other, tarry, products. A related reaction occurs between phenols and 3-amino-1*H*-isoindolone.

WHEN phthalodinitrile is heated in an excess of phenol, ammonia is evolved after about ca. 2 hours and up to 1 mol. can be driven off by prolonged heating.¹ The other products of the reaction include tarry, possibly polymeric, materials and small quantities of phthalocyanine. If the reaction is stopped after 1 hour when only a negligible amount of ammonia has been produced, 3-amino-1,1-di(hydroxyphenyl)-1*H*-isoindoles, (I) and (II), can be isolated.

The structures (I) and (II) are based on the chemical and spectral properties of the compounds. Both are soluble in dilute acids and aqueous sodium hydroxide but not in aqueous sodium carbonate. When heated with alkali, compound (I) is hydrolysed to give equimolar quantities of phenolphthalein imide and ammonia, while compound (II) gives the isomeric imide (VI).² Determination of active hydrogens with lithium aluminium hydride gives values of four and three for compounds (II) and (VI) respectively, while (I) reacts slowly and incompletely with this reagent.



The i.r. spectrum of (I) shows a broad absorption band in the 3000—3500 cm.⁻¹ region, but a peak at 1645 cm.⁻¹ may be assigned to the NH₂ deformation frequency³ as this is not present in related compounds formed from (I) with elimination of ammonia; the peak at 1682 cm.⁻¹ is assigned to the C=N stretching frequency. The presence of both *ortho*- and *para*-substituted aromatic rings is indicated by peaks at 750 and 835 cm.⁻¹, the absorption of the latter being more intense than that of the former. The i.r. spectrum of (II) is similar to that of (I) but differs in the relative intensities of the bands at 760 and 840 cm.⁻¹; the former in this case is more intense than the latter and is consistent with more *ortho*- substitution than in (I). The n.m.r. spectrum of (I) in dimethyl sulphoxide shows a symmetrical pattern of four peaks, characteristic of an A_2B_2 grouping (centred at τ 3·1) and a more complex pattern of roughly half the relative intensity (centred at τ 2·4). Similar absorptions are found in the spectra of phenolphthalein and its imide and are assigned respectively to the protons on the *para*- and ortho- substituted aromatic nuclei. The n.m.r. spectra of (II) and its hydrolysis product are similar to those of (I) and phenolphthalein imide in the τ 2·4 region, but the absorptions centred at τ 3·1 are more complex as would be expected for combinations of differently substituted nuclei.

Structures (I) and (II) are shown as amino-forms with endocyclic C=N bonds. The tautomeric imino-forms with exocyclic double bonds are also possible structures, but the data available are not sufficient for making definite conclusions about the fine structure of the compounds.

Compounds (I) and (II) are also obtained as a mixture of their hydrochlorides by treating a mixture of phthalodinitrile and phenol in chloroform with hydrogen chloride. A similar mixture appears to have been obtained from 3-amino-1,1-dichloro-1*H*-isoindole hydrochloride (VII) (produced by the action of hydrogen chloride on phthalodinitrile) by treatment with phenol in the presence of anhydrous aluminium chloride.⁴ Phenol and phthalodinitrile fail to condense under alkaline conditions. Phthalodinitrile has been condensed with alcohols both under acid 5 and alkaline 6 conditions to give 3-amino-1,1-dialkoxy-1*H*-isoindoles and it is possible that attack on phenol is initially at the hydroxy-group to give phenoxy-derivatives which undergo rearrangement to the hydroxyphenyl compounds. Although no reaction occurs when phthalodinitrile is heated with anisole, on treatment in chloroform with hydrogen chloride the product is mainly the hydrochloride (VII). An attempt to prepare the diphenoxy-compound by treatment of (VII) with phenol in the presence of a tertiary base was unsuccessful. A previous attempt ⁴ with anhydrous sodium phenoxide was also unsuccessful.

Compounds corresponding to (I) and (II) are not obtained upon heating phthalodinitrile with *para*-cresol or 2,6-xylenol since there is no well defined period when

¹ D. I. Packham, unpublished results.

² W. R. Orndorff and W. R. Barratt, J. Amer. Chem. Soc., 1924, **46**, 2483.

³ L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Methuen, London, 1958, p. 255.

⁴ M. E. Baguley, Ph.D. Thesis, London University, 1955.

J. A. Elvidge and R. P. Linstead, J. Chem. Soc., 1952, 5000.
F. Baumann, B. Biernert, G. Rösch, H. Vollmann, and W.

⁶ F. Baumann, B. Biernert, G. Rösch, H. Vollmann, and W. Wolf, *Angew. Chem.*, 1956, **68**, 133.



mixed with a small quantity of 3-amino-1,1-bis-(4hydroxy-3,5-dimethylphenyl)-1H-isoindole hydrochloride. The low yield may be due to steric hindrance to the initial attack on the hydroxy-group by the adjacent methyl groups. The xylenol derivative has a structure analgous to that of (I), as is shown by its ready hydrolysis to ammonia and 2,6-xylenolphthalein imide, which was related to the known phthalein by further partial hydrolysis. The compound obtained as its hydrochloride from para-cresol and phthalodinitrile in the presence of hydrogen chloride is assigned structure (IV) since it contains only three active hydrogen atoms and, on hydrolysis with alkali, gives 2 molar proportions of ammonia, and the known o-(2-hydroxy-5-methylbenzovl)benzoic acid (VIII). Compound (IV), therefore, appears to represent an intermediate stage in the suggested rearrangement of the di(aryloxy)- to the di-(hydroxyaryl)-compounds. However, the n.m.r. spectrum of the cresol derivative in pyridine shows only one methyl resonance at τ 7.95, whereas two types of absorption would be expected for structure (IV). Although structures (IV) and (II) have asymmetrically substituted carbon atoms, no attempt has been made to resolve these compounds into their enantiomers.

When phthalodinitrile is heated in phenol for several hours, up to 1 mol. of ammonia is evolved and it is possible to obtain a mixture of isomers of composition $[C_6H_4(CN)_2 + 3C_6H_5OH - NH_3]$ from the resulting tar. A similar mixture is obtained when compound (I) is heated with phenol. Determination of the number of active hydrogen atoms gives a value of 3, consistent with their formulation as 1,3,3-tri(hydroxyphenyl)-1H-isoindoles with structure (III) for one of the isomers and corresponding structures based on (II) and orthohydroxyphenyl groups for the others. The isomers may be partially separated by extraction with benzene, when the i.r. spectra of the residue and the microcrystalline powder which separates from the extract are similar and only differ in the relative intensities of the bands at 840 and 750 cm.⁻¹. Since compounds (I) and (II) have

phenolic groups, self-condensation through the aminogroup could lead to the tars or polymeric materials which are the other products of the reaction. A small quantity of a compound of composition $[C_6H_4(CN)_2 +$ $3CH_3C_6H_4OH - NH_3$ was obtained from phthalodinitrile and para-cresol and, since this has three active hydrogens, it appears to be 1,3,3-tri-(2-hydroxy-5-methylphenyl)-1H-isoindole with a structure analogous to (III) with the cresol groups linked through the positions ortho to the hydroxy-groups. Although ammonia was given off when (IV) was heated with cresol and when phthalodinitrile was heated with 2,6-xylenol, no products analogous to (III) could be identified. The reaction between 2,6-xylenol and 3-amino-1,1-bis-(4-hydroxy-3,5dimethylphenyl)-1*H*-isoindole gave a small quantity of material which was found (mass spectrometry) to contain a compound of composition $[C_6H_4(CN)_2 +$ $3(CH_3)_2C_6H_3OH - NH_3$].

In order to investigate the nature of the reaction between phenols and amino-1H-isoindoles experiments have been carried out on the model compound 3-amino-1H-isoindolone (V). This compound reacts with a 2 molar proportion of phenol with the liberation of 1 mol. of ammonia. With phenol, the product is the imide (VI), identical with the hydrolysis product of (II); no evidence for the production of other isomers was obtained. Similarly, the product from 2,6-xylenol is 2,6-xylenolphthalein imide. para-Cresol gives the xanthen derivative (IX) by internal condensation of the ortho-hydroxy-groups. The structure of (IX) is confirmed by a determination of the number of active hydrogen atoms (one) and by mass spectrometry which shows a parent peak at 327, with no peak at 345 and no metastable peak at 309.9 corresponding to the dehydration of the dihydroxy-compound to the xanthen. The condensation of geminal ortho-hydroxyphenyl groups to xanthens in the presence of dehydrating agents (e.g. in the preparation of fluorescein), is common, but such a condensation in the absence of a dehydrating agent is noteworthy; apparently it does not necessarily take place when phthalodinitrile is heated with *para*-cresol since the isolated product in this case has three active hydrogen atoms.

It is not clear why two molecules of phenol should condense with the amino-1H-isoindole group of (V) while only one molecule of phenol condenses with the amino-1H-isoindole group of (I) and (II). It seems unlikely that this is related to different ratios of aminoand imino-tautomers in the 1H-isoindole derivatives since the attack of phenol on the C=N group would give similar intermediates in each case. A mixture of products similar to that obtained from phthalodinitrile is also produced when 3-amino-1-imino-1H-isoindole is heated with phenol. It is likely in this case that the 1H-isoindole derivative initially dissociates into phthalodinitrile and ammonia.⁷

When compound (V) is heated with anisole, 0.5 mol.

⁷ J. D. Davies and D. I. Packham, unpublished results.

of ammonia is evolved and the self-condensation product (X) is formed. There appears to be no reason why compounds (I) and (II) should not undergo a similar self-condensation, but such a reaction seems to play little part in the formation of ammonia in the phenol-phthalodinitrile system since up to 1 mol. of ammonia can be liberated.

EXPERIMENTAL

Phthalodinitrile was recrystallised from benzene before use and phenols were distilled in a nitrogen atmosphere. Active hydrogen was determined by treatment of compounds with lithium aluminium hydride in diglyme and measurement of the volume of hydrogen produced.⁸ I.r. spectra were measured as KBr discs. Other physical measurements were made by Mr. H. M. Paisley (mass spectrometry), Dr. R. R. Dean (n.m.r.), and Mr. M. A. Francis differential thermal analysis (d.t.a.).

Thermal Reactions of Phthalodinitrile with Phenols.-*Phenol.* (a) Phthalodinitrile (5.12 g.) and phenol (50 ml.) were heated under reflux in a stream of nitrogen. After ca. 2 hr. ammonia (identified as the toluene-p-sulphonamide) began to be evolved and was titrated against standard acid. After $3\frac{1}{2}$ hr. 0.5 mol. of ammonia had been evolved but the reaction then slowed and a further 0.5 mol. was evolved only after ca. 52 hr. Most of the excess of phenol was distilled off under reduced pressure and the black tarry residue was extracted with benzene. Addition of light petroleum to the benzene extract precipitated (6 g.) a yellow, microcrystalline mixture of 1,3,3-tri(hydroxyphenyl)-1H-isoindoles, m.p. 140° (decomp.) [Found: C, 79.8; H, 4.8; N, 3.6%; M(Mechrolab osmometer, pyridine), 390. Calc. for $C_{26}H_{19}NO_3$: C, 79.45; H, 4.8; N, 3.6%; M, 393]; d.t.a. showed several ill-defined endotherms.

A similar product was obtained when 3-amino-1-imino-1H-isoindole ⁵ was used in place of phthalodinitrile.

(b) Phthalodinitrile (12.8 g.) and phenol (200 ml.) were heated under reflux for 1 hr. in a stream of nitrogen. Ammonia (0.004 mol.) was evolved. The black tar which remained after removal of most of the excess of phenol was heated with chloroform and a greyish brown powder (22 g.) was filtered off. The filtrate was extracted with sodium hydroxide solution, dried, and evaporated, to give unchanged phthalodinitrile (1.5 g.). The sodium hydroxide solution was just acidified and then made alkaline with sodium carbonate, and the precipitate (5 g.) was filtered off, washed, and dried. The combined product (27 g.) was extracted successively with toluene (for ca. 12 hr.) and then methanol. A small quantity of a blue pigment remained in the Soxhlet thimble. Concentration of the methanol extract gave 3-amino-1,1-di-(p-hydroxyphenyl)-1H-isoindole (I) (5.25 g.), which was crystallised from methanol [Found: C, 75.8; H, 4.9; N, 8.8%; M, (Mechrolab osmometer, pyridine) 317.6 (mass spectrometer), 316·121. $C_{20}H_{16}N_2O_2$ requires C, 75·95; H, 5·1; N, 8·9%; M, 316·1212]. The compound did not melt below 360° but became a black char at $ca. 290^{\circ}$; d.t.a. showed a sharp endotherm at 292°. Concentration of the toluene extract gave a brown powder (7 g.) which was dissolved in hot n-hydrochloric acid (500 ml.), and the solution, after being decolourised with active charcoal, was treated with aqueous sodium carbonate. The off-white precipitate (5 g.) crystallised from toluene to give 3-amino-1-(o-hydroxyphenyl)-

1-(p-hydroxyphenyl)-1H-isoindole (II) (2.5 g.), and a small quantity of material not readily soluble in toluene which was identified as the di(p-hydroxy)-isomer (I). Crystallisation from hydrochloric acid gave the hydrochloride, m.p. 215° (decomp.) (Found: C, 65.9; H, 4.9; Cl, 9.6; N, 8.0. $C_{20}H_{16}N_2O_2$, HCl, $\frac{1}{2}H_2O$ requires C, 66.4; H, 5.0; Cl, 9.85; N, 7.75%); treatment of this compound with aqueous sodium carbonate, gave the partly hydrated freebase, m.p. 195° (decomp.), d.t.a. endotherm 196° (Found: C, 74.0; H, 5.2; N, 9.2. Calc. for $C_{20}H_{16}N_2O_2,H_2O$: C, 71.9; H, 5.4; N, 8.4%). Recrystallisation from toluene gave the anhydrous compound, m.p. 145° (decomp.), d.t.a. endotherm 141° [Found: C, 75.9; H, 5.1; N, 8.8%; M(mass spectrometry), 316·1215; Active H, 3·9. $C_{20}H_{16}N_2O_2$ requires C, 75.95; H, 5.1; N, 8.9%; M 316.1212; Active H, 4].

(c) 3-Amino-1,1-di-(p-hydroxyphenyl)-1H-isoindole (I) (3·2 g.) was heated in phenol (60 ml.) for 60 hr.; ammonia (0·91 mol.) was given off. Phenol was removed under reduced pressure and the residual tar was heated with benzene until a yellow powder was obtained. This was extracted in a Soxhlet apparatus with toluene; the microcrystalline powder which separated from the extract was similar to that previously obtained from phthalodinitrile after being heated for a prolonged period in phenol [Found: C, 79·2; H, 4·8; N, 3·8%; M(mass spectrometer), 393·1390. Calc. for C₂₆H₁₉NO₃: C, 79·45; H, 4·8; N, 3·6%; M, 393·1365]. Determination of active hydrogens gave a value of 2·9.

p-Cresol. Phthalodinitrile (12.5 g.) and para-cresol (250 ml.) were heated under reflux. As soon as the mixture reached the boiling point ammonia was detected; the heating was continued until 1 mol. had evolved. After removal of most of the excess of cresol the tarry residue was taken up in ether; addition of light petroleum gave a yellowish brown precipitate, which was repeatedly taken up in benzene and reprecipitated with light petroleum. The product, 1,3,3-tri-(2-hydroxy-5-methylphenyl)-1H-isoindole, was obtained as a red-orange microcrystalline powder, m.p. 270° (decomp.) (Found: C, 80.5; H, 5.6; N, 3.5. C₂₉H₂₅NO₃ requires C, 80.0; H, 5.75; N, 3.2%); active hydrogen determination gave a value of 3.2. The mass spectrum of the compound did not exhibit a parent peak, but two peaks corresponding to loss of one and two hydrogen atoms respectively were present (Found: M - 1, 434·1725; M - 2, 433·1678. C₂₉H₂₄NO₃ requires $434 \cdot 1756.$ C₂₉H₂₃NO₃ requires 433.1678).

2,6-Xylenol. Ammonia was slowly evolved when phthalodinitrile was heated in 2,6-xylenol, however, when the reaction was stopped after 6 hr. (0.005 mol. of ammonia evolved) much unchanged phthalodinitrile was recovered. When the mixture was heated for 50 hr. (0.7 mol. of ammonia evolved) the black tar which was produced was soluble in benzene to leave a residue of phthalocyanine; no other identifiable products were obtained.

Hydrogen Chloride-catalysed Reactions of Phthalodinitrile with Phenols.—Phenol. A cooled solution of phenol (40 g.) and phthalodinitrile (25.6 g.) in dry chloroform (400 ml.) was saturated with dry hydrogen chloride and set aside for a week. The mixture of hydrochlorides (79 g.) which were produced was filtered off and dried in a stream of nitrogen (Found: C, 61.4; H, 4.7; Cl, 16.9; N, 6.5. Calc. for $C_{20}H_{16}N_2O_2$,HCl: C, 68.1; H, 4.8; Cl, 10.1; N, 7.9. ⁸ F. Wild, 'Estimation of Organic Compounds,' Cambridge

University Press, Cambridge, 1953, p. 86.

Calc. for $C_{20}H_{16}N_2O_2, 2HCl: C, 61.7$; H, 4.6; Cl, 18.2; N. 7.2%). The hydrochlorides (13 g.) were dissolved in water, the small quantity of insoluble material was filtered off, and aqueous sodium carbonate was added to the filtrate. The precipitated product (8.7 g.) (Found: C, 75.0; H, 5.0; N, 8.7%) was extracted with toluene for *ca*. 8 hr. and the toluene extract was concentrated to 200 ml.; when cooled, this gave 3-amino-1-(p-hydroxyphenyl)-1-(*o*-hydroxyphenyl)-1*H*-isoindole (II) (4.5 g.) which was purified *via* the hydrochloride as previously described. The residue from the toluene extract was recrystallised from methanol to give 3-amino-1,1-di-(p-hydroxyphenyl-1*H*-isoindole (I) (3.5 g.).

para-Cresol. Phthalodinitrile (12.8 g.) and *para-cresol* (22 g.) in chloroform (200 ml.), treated as for phenol, gave the *hydrochloride*, m.p. 215° (decomp.) (20.4 g., 54%) (Found: C, 69.3; H, 5.5; Cl, 9.7; N, 7.7. $C_{22}H_{21}ClN_2O_2$ requires C, 69.5; H, 5.5; Cl, 9.3; N, 7.4%). The precipitate obtained from the hydrochloride (7.61 g.) and aqueous sodium carbonate was recrystallised from benzene giving 3-amino-1-(p-tolyloxy)-1-(2-hydroxy-5-methylphenyl)-1H-

isoindole (IV) (6.5 g., 94%), m.p. 220° (decomp.) [Found: C, 76.6; H, 5.8; N, 8.2%; M(mass spectrometry), 344.1536; Active H, 3.2. $C_{22}H_{20}N_2O_2$ requires C, 76.75; H, 5.8; N, 8.1%; M, 344.1525; Active H, 3].

The 1H-isoindole derivative was heated with *para*cresol for 54 hr. Ammonia (1 mol.) was evolved but no identifiable products were obtained from the tarry product.

2,6-Xylenol. Phthalodinitrile (12.8 g.) and 2,6-xylenol (25 g.) in chloroform (200 ml.) on treatment with hydrogen chloride gave, after 3 weeks, a mixture (8.4 g.) of hydrochlorides (Found: C, 52.4; H, 3.9; Cl, 24.0; N, 13.7%). Unchanged phthalodinitrile and xylenol were recovered from the reaction mixture after removal of the hydrochlorides. The mixture of hydrochlorides (6 g.) was heated with water (350 ml.) and cooled; phthalimide (2.0 g.) was filtered off and aqueous sodium carbonate was added to the filtrate. The precipitate (1.8 g.) was recrystallised from ethanol to give 3-amino-1,1-di-(4-hydroxy-3,5-dimethylphenyl)-1H-isoindole, m.p. 233° (decomp.) (Found: C, 77.2; H, 6.4; N, 7.7%; Active H, 4.0. $C_{24}H_{24}N_2O_2$ requires C, 77.5; H, 6.45; N, 7.5%; Active H, 4).

The 1*H*-isoindole derivative (1·24 g.) was heated for 40 hr. in 2,6-xylenol (25 ml.); ammonia (0·94 mol.) was evolved. The black tar produced was taken up in ether, the solution was decolourised with active charcoal, and a small quantity of yellow powder was precipitated by addition of light petroleum. Mass spectrometry indicated the presence of the tri(hydroxyaryl)-1H-isoindole analogous to those obtained from phenol and *para*-cresol (Found: *M*, 477·2309, Calc. for $C_{32}H_{31}NO_3$: *M*, 477·2304).

Reactions of Phenols with 3-Amino-1H-isoindolone.— 3-Amino-1H-isoindolone was prepared by thermal cyclisation of ortho-cyanobenzamide⁹ and was purified by sublimation.

Phenol. 3-Amino-1*H*-isoindolone (14.6 g.) and phenol (250 ml.) were heated during 20 hr. when ammonia (0.93 mol.) was evolved. Most of the excess of phenol was removed under reduced pressure and the residue crystallised from aqueous ethanol to give the imide (VI) (22 g., 70%), m.p. 268° (decomp.) (lit.,² m.p. 269-270°), mixed m.p.

with phenolphthalein imide, 254° [Found: C, $75\cdot9$; H, $4\cdot8$; N, $4\cdot7_{\circ}$; M(mass spectrometer), $317\cdot097$; Active H, $2\cdot8$. Calc. for C₂₀H₁₅NO₃: C, $75\cdot6$; H, $4\cdot7$; N, $4\cdot4_{\circ}$; M, $317\cdot105$; Active H, 3].

para-Cresol. This gave ammonia (0.94 mol.) and a tar from which the xanthen (IX) (28%) was obtained by trituration with ether and recrystallisation from aqueous ethanol, m.p. 208° (decomp.) [Found: C, 80.3; H, 5.4; N, 4.6%; M(mass spectrometer), 327.1254; Active H, 1.1. $C_{22}H_{17}NO_2$ requires C, 80.8; H, 5.2; N, 4.3%; M, 327.1259; Active H, 1]. The compound was unaffected upon being heated under reflux in aqueous alkali or dilute ethanolic hydrochloric acid.

2,6-Xylenol. This gave ammonia (0.94 mol.) and 2,6-xylenolphthalein imide (65%), m.p. 314° (decomp.) (from benzene-ethanol) (Found: C, 77.3; H, 6.1; N, 3.6. $C_{24}H_{23}NO_3$ requires C, 77.25; H, 6.2; N, 3.75%).

Hydrolyses.—Hydrolyses were generally carried out with 2N-sodium hydroxide. Ammonia was titrated against standard acid and the other products were obtained by acidification of the reaction solution.

(a) 3-Amino-1,1-di-(p-hydroxyphenyl)-1H-isoindole (I) (1.58 g.) gave ammonia (0.96 mol.) during 2 hr. and phenolphthalein imide (1.2 g., 76%), m.p. 282° (decomp.) (from aqueous ethanol) (Found: C, 75.9; H, 4.7; N, 4.4. Calc. for C₂₀H₁₅NO₃: C, 75.6; H, 4.7; N, 4.4%), identical with a sample obtained by treating phenolph thalein with concentrated aqueous ammonia.*

(b) 3-Amino-1-(o-hydroxyphenyl)-1-(p-hydroxyphenyl)-1H-isoindole (II) (1·16 g.) gave ammonia (0·94 mol.) and the imide (VI) (1·16 g. 100%), identical with the compound obtained from 3-amino-1H-isoindolone and phenol. Further hydrolysis of the imide (VI) with 5N-sodium hydroxide gave a slow evolution of ammonia (0·3 mol. in 10 days) and the product appeared to be a mixture of the imide (VI) and the parent phthalein (Found: N, 2·5%). The imide (VI) was fused with potassium hydroxide at 180° for 8 hr., the mixture was poured into water, acidified, and steam distilled to give a small quantity of benzoic acid; the residue appeared to be unchanged imide and no other compounds were identified.

(c) 3-Amino-1,1-di-(4-hydroxy-3,5-dimethylphenyl)-1*H*isoindole (0.465 g.) gave ammonia (1.02 mol.) and 2,6-dimethylphenol phthalein imide (0.46 g., 98%) identical with the product of the reaction between 2,6-xylenol and 3-amino-1*H*-isoindolone. Further hydrolysis with 2Nsodium hydroxide during 96 hr. gave ammonia (0.7 mol.) and a mixture of 2,6-xylenolphthalein and its imide (Found: N, 0.95%); the last two compounds were identified by comparison of i.r. spectra with those of the imide and authentic 2,6-xylenolphthalein.¹⁰

(d) 3-Amino-1-(p-tolyloxy)-1-(2-hydroxy-5-methylphenyl)-1*H*-isoindole (IV) (3·44 g.) gave ammonia (1 mol. during 100 min., 1·88 mol. during 55 hr.) and 2-(2-hydroxy-

5-methylbenzoyl)benzoic acid (VIII) (1.98 g., 77.5%), m.p. 194° (Found: C, 70.4; H, 4.7. Calc. for $C_{15}H_{12}O_4$: C, 70.35; H, 4.7%), identical with an authentic specimen.¹¹ Ether extraction of the acidified filtrate gave *para*-cresol.

Experiments with Anisole.—No ammonia was given off when phthalodinitrile was heated with anisole and the nitrile was recovered unchanged.

Phthalodinitrile and anisole in chloroform when treated

^{*} As reported for the imide (VI) (ref. 2).

⁹ A. Braun and J. Tcherniac, Ber., 1907, 40, 2709.

¹⁰ G. Zigeuner and E. Ziegler, Monatsh., 1948, 79, 371.

¹¹ W. H. Bentley, H. D. Gardner, and C. Weizmann, J. Chem. Soc., 1907, **91**, 1626.

with dry hydrogen chloride gave a precipitate of a hydrochloride (Found: C, 44.9; H, 3.7; Cl, 33.8; N, 12.6%) which gave phthalimide when treated with water.

When 3-amino-1*H*-isoindolone (1·46 g.) was heated in anisole (25 ml.) for 63 hr. ammonia (0·49 mol.) was evolved; concentration of the solution and addition of light petro-leum gave di-(1-oxo-1H-indol-3-yl)amine (X) (1·1 g., 80%), m.p. 273° (decomp.) (from benzene) [Found: C, 69·3; H 3·3; N, 15·0%; M(mass spectrometer), 275·0688. C₁₆H₉N₃O₂ requires C, 69·9; H, 3·3; N, 15·25%; M,

275.0695]. The same compound was obtained when anisole was replaced by *o*-dichlorobenzene.

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