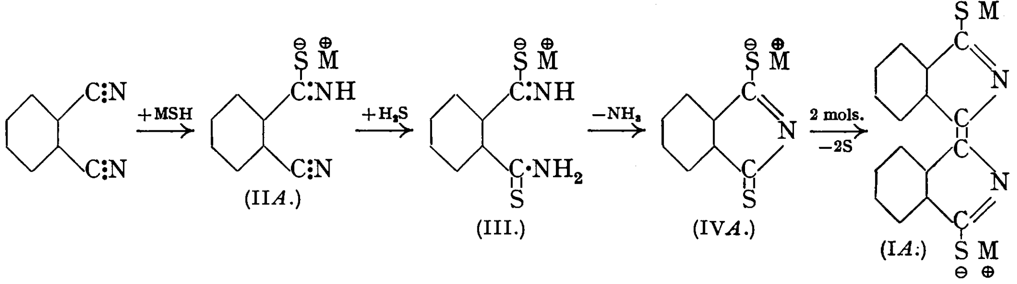
114. *Dithio-β-*iso*indigo. Part II. Mechanism of its Formation from Phthalonitrile. Derivatives.*

By H. D. K. Drew and D. B. Kelly.

Experimental results are given in support of the hypothesis that dithio-β-*iso*indigo is formed from phthalonitrile and hydrogen sulphide, in the presence of ammonia or alkali, through the stages of o-*cyanothiobenzamide* and dithiophthalimide. Thiophthalimidine is described, together with its conversion into dithio-β-*iso*indigo. Further experiments are described, the results of which tend to strengthen the evidence previously given as to the structure of dithio-β-*iso*indigo.

The mechanism of the formation of dithio-β-*iso*indigo (I) from phthalonitrile and hydrogen sulphide in the presence of aqueous or alcoholic ammonia or alkali (Drew and Kelly, preceding paper) has been further studied. It now seems clear, on the evidence which follows, that o-*cyanothiobenzamide* (II) and dithiophthalimide (IV) are intermediate products, and there is evidence to show that both of these substances, and also the final product itself, are generated initially as their ammonium or alkali salts. The following mechanism is suggested as probable (M = NH_4 or Na) :



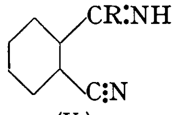
The main product of the action of aqueous-alcoholic ammonium hydrosulphide on phthalonitrile at room temperature was found to be o-cyanothiobenzamide (II), a substance which had already been discovered (Imperial Chemical Industries, Dyestuffs Group; private communication) but has not yet been described in the literature; the by-product of the reaction was (I). Ammonium hydrosulphide had no action upon phthalonitrile in dry benzene, even on long boiling; but the addition of a little alcohol caused the reaction to set in immediately. Ammonia was without action upon phthalonitrile in hydroxylic or in non-hydroxylic solvents under the conditions studied by us (*e.g.*, in alcohol or in benzene, at the boiling point of the solvent); normal sodium sulphide did not change phthalonitrile into (II); and hydrogen sulphide did not react with phthalonitrile in non-hydroxylic solvents.

The production of (II) from phthalonitrile, therefore, requires the presence of a hydroxylic solvent and is greatly facilitated by the presence of a base (though, as will appear later, aniline can take the place of both together), conditions which are required also for the preparation of (I) from phthalonitrile. It can be inferred both that (II) is an intermediate in the production of (I), and that a hydrosulphide of a base is the initial agent of the change. The addition of a hydrosulphide molecule at one of the cyano-groups would produce the *iso*thioamide salt (II*A*); and, if it be assumed that the remaining *o*-cyano-group is thus activated and enabled to attach a molecule of hydrogen sulphide (or two molecules of the hydrosulphide, with subsequent elimination of a molecule of the normal sulphide), a salt (III) of phthalodithioamide would be produced. The elimination of a molecule of ammonia from this would result in ring closure to a salt (IV*A*) of dithiophthalimide. Both *o*-cyanothiobenzamide and dithiophthalimide readily form salts in alkaline media; when the free substances are synthesised from phthalonitrile in aqueous media, they separate from solution only after some time has elapsed since their formation was indicated by the change of colour of the reaction mixture, and they must therefore have been present as soluble salts. The same applies also to (I).

The feasibility of considering *o*-cyanothiobenzamide as an intermediate in the preparation of (I) from phthalonitrile was shown by the fact that (II) was quantitatively transformed into (I) on treatment with ammonia and hydrogen sulphide in aqueous or alcoholic solution, but not in dry benzene. Moreover, in the transformation of (II) into (I), dithiophthalimide was isolated as an intermediate product, working with a limited proportion of ammonia in benzene–alcohol as solvent.

We have already shown (*loc. cit.*) that dithiophthalimide (IV) is converted into (I) on being heated with silver powder, or on being treated with alcoholic ammonia in the presence or absence of hydrogen sulphide; and it has now been found that this change may also be brought about either by treatment of (IV) with aqueous or alcoholic caustic alkali or by simply heating the dry substance at 180—200°. All the above methods lead to practically quantitative yields of (I). The conversion of two mols. of dithiophthalimide (in the form of a salt, IV*A*) into a mol. of (I*A*) involves the direct elimination of two atoms of sulphur. The ***disodium*** salt of (I) was in fact prepared as a ***tetrahydrate***, soluble in alcohol or in aqueous alkali and readily decomposable into (I) by carbonic acid. In the transformations carried out in the presence of bases, the eliminated sulphur was obtained either wholly in the free state or in part also as polysulphide. A precedent for this type of reaction is found in the spontaneous conversion of α-thioisatin into indigotin and sulphur (*Centr.*, 1902, I, 1429), a change which is facilitated by the presence of alkali.

Two alternative possibilities in regard to the initial change in the reaction with phthalonitrile were considered: (*a*) that a solvent molecule (water or alcohol) might first have been added at one of the cyano-groups, giving *o*-cyanobenzamide (V; R = OH) or its *O*-ether (V; R = OEt); but this was shown not to be the case, since *o*-cyanobenzamide did not react with ammonia and hydrogen sulphide either in water or in alcohol; (*b*) that a molecule of ammonia might similarly have been added at a cyano-group, giving rise to the amidine



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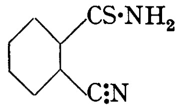

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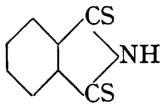
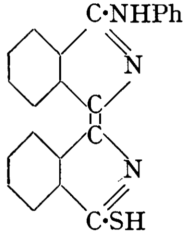


(IV.)

(V; R = NH_2), the action of hydrogen sulphide then causing replacement of the imino-group by a sulphur atom (a reaction known to occur readily with imino-ethers in ethereal solution); but this mechanism was likewise eliminated, from the consideration that neither (II) nor (I) could be produced from phthalonitrile with ammonia and hydrogen sulphide in non-hydroxylic solvents.

In order to obtain confirmation of the mechanisms of reaction suggested above, the action of hydrogen sulphide on phthalonitrile in the presence of aniline was examined. In boiling alcohol as solvent, the sole product of the reaction was (I), showing that aniline can take the place of ammonia; but when hydrogen sulphide was passed into a gently boiling mixture of aniline and phthalonitrile, the *monophenylimine* (VI) of thio-β-*iso*indigo and the *diphenylimine* (VII) of β-*iso*indigo were produced as highly coloured, crystalline substances. These two substances were probably generated from preformed (I) and aniline, since (VII) resulted only after prolonged boiling of the reaction mixture and since *thiophthalimidemonophenylimine* (VIII), which was prepared from dithiophthalimide and aniline, was shown to remain unchanged on being warmed with alcoholic ammonia. However (VIII) was produced, as the chief product, when phthalonitrile was treated with hydrogen sulphide in a boiling mixture of xylene and aniline; under these conditions, preformed dithiophthalimide evidently interacted with aniline, in preference to undergoing the loss of sulphur and conversion into (I). The results of these interactions of phthalonitrile and hydrogen sulphide in the presence of aniline are consistent with the foregoing suggestions in the case of ammonia, the aniline evidently acting, prior to the formation of dithiophthalimide, as the necessary basic constituent of the reaction mixture and not as a condensing reagent; at the same time it is manifest that the aniline acts also in place of the hydroxylic solvent which appears essential when ammonia is used as the base.



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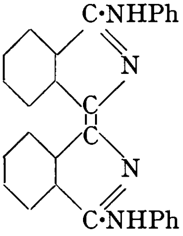

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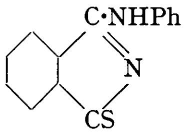

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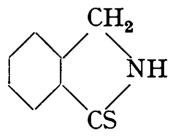
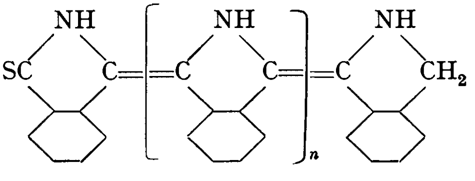


(IX.)

A number of unsuccessful methods were tried for the preparation of *thiophthalimidine* (IX), but the substance, which proved to be colourless, was eventually obtained in good yield by the reduction of dithiophthalimide with tin and hydrochloric acid. On being heated below 200° with sulphur, (IX) was transformed into (I) and hydrogen sulphide, the reaction supplying further evidence in favour of the structure proposed for (I). Only a very small proportion of (IX) was produced from phthalimidine and phosphorus pentasulphide.

When (IX) was heated alone at 170°, self-condensation occurred with elimination of hydrogen sulphide and production of a brownish-black *substance* which appeared to consist of a large number of molecules of thiophthalimidine condensed together as shown in (X); analysis indicated $n = 11$ (approx.). One of the products of the action of copper powder on dithiophthalimide was indicated by its properties to be of the same type as (X).



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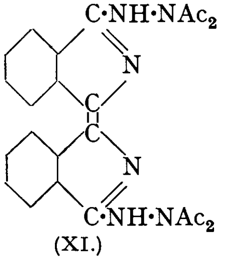

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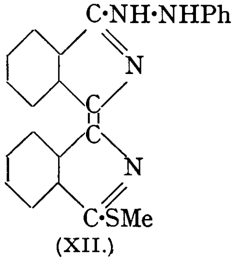
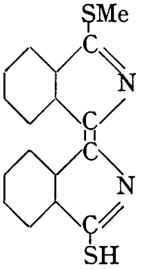


(XII.)

Some further work has been carried out on the hydrazine derivatives and on the *S*-alkyl derivatives of (I). The structure of the dihydrazone prepared (*loc. cit.*) from dithio-β-*iso*indigo has been confirmed by the preparation of its yellow tetra-acetyl derivative (XI), and of its highly dichroic (green-red) *dibenzylidene* and *di*-p-*anisylidene* derivatives. The *monophenylhydrazone* from (I) was violet-black and its S-*methyl* derivative (XII) consisted of red needles. The mono- and the di-phenylimine (VI and VII) were produced on boiling a solution of (I) in aniline for a short and a long period, respectively; they were dichroic (green-red); the S-*methyl* derivative of (VI) was brown. S-*Methyldithio*-β-iso*indigo* (XIII), consisting of very dark reddish-brown crystals, was obtained by the action of methyl iodide (1 mol.) on the disodium salt of (I) in alcohol; ethylation of (XIII) gave S-*methyl*-S′-*ethyldithio*-β-iso*indigo* (XIV), which was pale yellow.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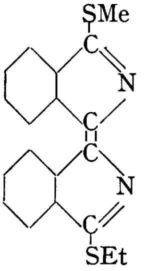
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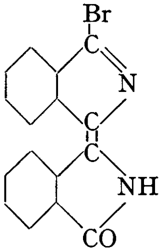
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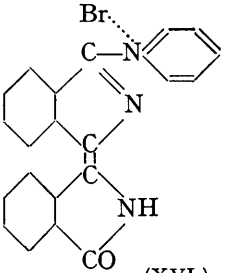
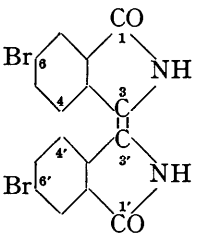

(XVI.)

Only indirect evidence of the presence of an ethylenic double bond in the structure of dithio-β-*iso*indigo having been obtained so far, the action of bromine on (I) was examined. However, the product of the action of cold bromine vapour on (I) was 1-*bromo*-3-*phthalimidyl*iso*indolenine* (XV), as was shown by its conversion by means of aniline into the *monophenylimine* of β-*iso*indigo, which was obtained free and also as a crystalline addition compound with a molecule of ethyl alcohol. With pyridine, (XV) gave the brownish-red *pyridinium bromide* derivative (XVI) as the crystalline *trihydrate*, soluble in water. The action of bromine in chloroform upon *SS*′-dimethyldithio-β-*iso*indigo gave dark red needles of a *dibromide*, in which the bromine atoms may have been attached at the ethylenic double bond; this view seems more probable than that the bromine was added at one of the sulphur atoms, both because the addition of a further two bromine atoms at the remaining sulphur atom could not be effected and because the bromine could be quantitatively removed from the dibromide, by boiling with water or alkali, with regeneration of the original dimethyldithio-compound.

Bromine was without action upon β-*iso*indigo in the cold; but in a sealed tube at 100° it gave nuclear mono- and di-bromo-derivatives of β-*iso*indigo, with the bromine in the 6 : 6′- or 5 : 5′-positions, since 5-bromophthalimide was obtained on oxidation; the chief product was probably (XVII).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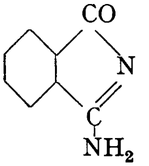
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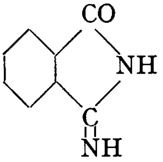
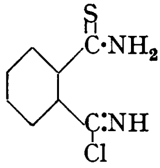

(XIX.)


(XX.)

Since dithiophthalimide was readily transformed into (I) by means of ammonia, the action of ammonia on monothiophthalimide was tried. In aqueous solution, hydrogen sulphide was split off from the first-formed ammonium salt and colourless crystals of *iminophthalimidine* (XVIII or XIX), readily soluble in hot water, were produced. By the action of heat upon *o*-cyanobenzamide, Braun and Tscherniac (*Ber.*, 1907, **40**, 2709) obtained a substance which they described as iminophthalimide; it had the same melting point as that of the substance described above but was "insoluble in water." The action of hydrogen chloride in benzene on *o*-cyanothiobenzamide gave a *hydrochloride* which is probably to be represented by (XX), since it was transformed by dry ammonia into the original thioamide and by water into monothiophthalimide.

EXPERIMENTAL.

o-*Cyanothiobenzamide* (II).—(*a*) A solution of phthalonitrile (5 g.) in hot alcohol (40 c.c.) was allowed to cool with stirring. A solution of sodium sulphide (10 g.) in water (10 c.c.) was saturated with hydrogen sulphide and added to the suspension of phthalonitrile. The whole was stirred (6 hours); from time to time the silky yellow needles of (II) were decanted from the heavy crystals of phthalonitrile, the decanted liquid filtered, and the filtrate returned to the reaction vessel. The product was washed with water, cold alcohol, and then warm benzene, to remove unchanged phthalonitrile. A final portion of (II) was obtained from the mother-liquor by passing in carbon dioxide. Yield, 2·4 g. (38%). For analysis (II) was crystallised from alcohol (Found : C, 59·0; H, 3·7; N, 17·3. $C_8H_6N_2S$ requires C, 59·3; H, 3·7; N, 17·3%); it was readily soluble in pyridine, aqueous sodium sulphide, or aqueous caustic alkalis, and was changed quantitatively to monothiophthalimide by warm dilute mineral acids or acetic acid; it softened at 216° and charred at 221—224°.

(*b*) Powdered phthalonitrile (2 g.), stirred for 8 hours at room temperature with alcohol (20 c.c.) and aqueous ammonia (*d* 0·88; 20 c.c.) previously saturated with hydrogen sulphide, gave pure (II) (yield, 1·1 g.), extracted by hot alcohol, and (I) (yield, 0·4 g.).

Preparation of Dithio-β-iso*indigo* (I) *from Phthalonitrile by Means of Aqueous Sodium Hydrosulphide.*—A mixture of phthalonitrile (1 part) and crystallised sodium sulphide (4 parts; 2 mols.) in water (20 parts) was saturated with hydrogen sulphide and then boiled under reflux for 2 hours. The solid product was filtered off and washed with hot water, alcohol, and carbon disulphide; it consisted of crystalline (I) in a very pure state (yield, 1 part: 90%). The *disodium* salt of (I) was obtained as a *tetrahydrate* by dissolving (I) (6 g.) in sodium hydroxide (10 g.) and water (20 c.c.) and warming; the paste was cooled in ice, and the solid filtered off and dried over potash. For analysis, a filtered solution in alcohol was precipitated with benzene; the salt consisted of brown micro-crystals, hydrolysed by water or carbon dioxide, but soluble in alcohol to an intensely red solution [Found : Na, 10·9; H_2O (loss at 120° in dry CO_2-free air), 17·6. $C_{16}H_8N_2S_2Na_2,4H_2O$ requires Na, 11·2; H_2O, 17·6%].

S-*Methyldithio*-β-iso*indigo* (XIII).—Alcoholic methyl iodide (75 c.c. of a 1% solution) was gradually added to a stirred solution of the hydrated disodium salt of (I) (5 g.) in alcohol (100 c.c.) : the brown precipitate was removed after 3 hours and fractionated from pyridine to remove the less soluble dimethylated compound. For analysis, (XIII) was crystallised from amyl alcohol and then from pyridine; it consisted of dark reddish-brown needles, m. p. 245° (Found : C, 66·4; H, 3·8; N, 9·5. $C_{17}H_{12}N_2S_2$ requires C, 66·2; H, 3·9; N, 9·1%); it dissolved in aqueous alcoholic caustic alkalis to deep reddish-brown solutions, and evolved methylthiol when heated with dilute mineral acids. Treatment of its solution in aqueous alcoholic sodium hydroxide with ethyl iodide gave S-*methyl*-S′-*ethyldithio*-β-iso*indigo* (XIV), which formed long, pale yellow needles, m. p. 152—153°, from alcohol (Found: C, 68·0; H, 4·8. $C_{19}H_{16}N_2S_2$ requires C, 67·8; H, 4·8%).

Thiophthalimidemonophenylimine (VIII) was prepared by heating together alcoholic dithiophthalimide and aniline for ½ hour. It separated from alcohol in flat, orange-brown needles, m. p. 209° (Found: C, 70·8; H, 4·7; N, 12·1. $C_{14}H_{10}N_2S$ requires C, 70·5; H, 4·2; N, 11·8%); it dissolved in hot aqueous sodium hydroxide (orange solution); warming with alcoholic ammonia did not change it.

Phthalimidemonophenylimine (VIII, with O instead of S), from monothiophthalimide and aniline, crystallised from alcohol in pale yellow needles, m. p. 161° (Found : C, 75·5; H, 4·8. $C_{14}H_{10}ON_2$ requires C, 75·6; H, 4·5%).

Thiophthalimidine (IX) was prepared by reducing powdered dithiophthalimide (1 part) with precipitated tin (5 parts) and concentrated hydrochloric acid (10 parts) at 100° (3 hours); when the solution was cooled in ice, yellow thiophthalimidine stannochloride separated. This was collected and boiled with water (50 parts), and the tin precipitated as sulphide. The filtrate (and extracts with boiling water of the precipitate) deposited (IX) in colourless plates (yield, 75%), m. p. 159° (Found : C, 64·5; H, 4·7; N, 9·4; S, 21·55. C_8H_7NS requires C, 64·4; H, 4·7; N, 9·4; S, 21·5%). When kept at 170° for 6 hours, (IX) evolved hydrogen sulphide and became converted into an insoluble black substance, possibly (X), which was purified by extraction with alcohol and hot pyridine and then precipitated from solution in warm concentrated sulphuric acid (Found : N, 10·2; S, 3·2%).

The action of phosphorus pentasulphide (5 parts) on phthalimidine (5 parts) in boiling dry benzene (100 parts) gave only a trace of thiophthalimidine, the main product being a very stable, dark blue, insoluble powder, which was extracted with boiling water, alcohol, and pyridine. For analysis, it was twice reprecipitated by means of ice from its blue-green solution in warm concentrated sulphuric acid (Found : C, 67·8; H, 3·9; N, 8·7; S, 9·3%). This *substance* was unmelted at 350° and was insoluble in hot aqueous alcoholic caustic alkalis; it was not identified and may not have been pure, but the empirical formula $C_{16}H_8O_2N_2S$ is provisionally suggested.

Thio-β-iso*indigomonophenylhydrazone* was prepared by boiling (I) (3 g.) with phenylhydrazine (10 g.) and alcohol (20 c.c.) for 18 hours : tough, violet-green needles separated (Found : C, 71·9; H, 4·4; N, 15·55; S, 8·5. $C_{22}H_{16}N_4S$ requires C, 71·7; H, 4·4; N, 15·2; S, 8·7%). It gave deep blue solutions in pyridine and aqueous-alcoholic caustic alkalis. Its S-*methyl* derivative (XII) was obtained, by the action of methyl iodide and aqueous alcoholic sodium hydroxide, in long, dark red needles (from pyridine), m. p. 220° (decomp.) (Found : C, 72·5; H, 4·4; N, 15·0. $C_{23}H_{18}N_4S$ requires C, 72·2; H, 4·5; N, 14·7%).

Thio-β-iso*indigomonophenylimine* (VI) was prepared by boiling (I) with aniline for 2½ hours; the isolated solid was extracted with boiling alcohol, and the extract allowed to cool; (VI) then separated in red needles with green reflex, m. p. 265° (Found : N, 11·65; S, 9·2. $C_{22}H_{15}N_3S$ requires N, 11·9; S, 9·1%); it gave intensely red solutions in bases. Its S-*methyl* derivative was obtained in brown needles from amyl alcohol, with which it crystallised; the solvent-free substance had m. p. 212° (Found : C, 74·6; H, 4·9. $C_{23}H_{17}N_3S$ requires C, 75·2; H, 4·7%). A small proportion of (VI) resulted on boiling crude (IX) with aniline for 3 hours; but purified (IX) was not observed to give this reaction.

β-iso*Indigodiphenylimine* (VII) was prepared from (I) and aniline, after boiling for 1 day; the red-green dichroic product was recrystallised from pyridine, with which it combined; boiling alcohol removed the pyridine, leaving brown needles, m. p. 306° (Found : C, 81·0; H, 5·1. $C_{28}H_{20}N_4$ requires C, 81·5; H, 5·2%).

From β-*iso*indigodihydrazone were prepared : (a) β-iso*indigodibenylidenedihydrazone*, dichroic (green-red) needles from alcoholic pyridine, m. p. 272° (Found : C, 76·8; H, 5·2; N, 17·9. $C_{30}H_{22}N_6$ requires C, 77·2; H, 4·7; N, 18·0%); (b) β-iso*indigodi*-p-*anisylidene-dihydrazone*, m. p. 259°, similar to the last substance (Found : C, 72·9; H, 5·3; N, 16·5. $C_{32}H_{26}O_2N_6$ requires C, 73·0; H, 5·0; N, 16·0%); (c) β-iso*indigotetra-acetyldihydrazone* (XI), by boiling (I) with pure acetic anhydride for 10 minutes; the product formed silky yellow needles from pyridine, m. p. 262° (Found : C, 63·0; H, 4·9; N, 17·5. $C_{24}H_{22}O_4N_6$ requires C, 62·9; H, 4·8; N, 17·5%); it was unchanged on being boiled with benzaldehyde.

1-*Bromo*-3-*phthalimidyl*iso*indolenine* (XV) was obtained on exposing (I) (5 g.) to bromine vapour for 2 days in a closed vessel. The excess of halogen was allowed to evaporate, the brick-red powder boiled with several portions of water, and the yellow residue dried at 110° and crystallised from a large volume of boiling xylene : yellow, silky needles were obtained (4 g.), m. p. 297° (Found : C, 59·6; H, 3·1; N, 9·0; Br, 24·7. $C_{16}H_9ON_2Br$ requires C, 59·1; H, 2·8; N, 8·6; Br, 24·6%). The substance crystallised well from chloroform, but appeared to retain the solvent. Oxidation of (XV) with chromic acid in acetic acid gave a small yield of phthalimide. The action of boiling alcoholic aniline on (XV) gave *monophenylimino*-β-iso*indigo mono-alcoholate*, forming brown needles from alcohol, m. p. 280° [Found : C, 75·0; H, 5·6; N, 11·5; C_2H_5·OH (loss at 130°), 11·9. $C_{22}H_{15}ON_3,C_2H_5\cdot OH$ requires C, 75·2; H, 5·5; N, 11·1; C_2H_5·OH, 12·0%]; it did not combine with amyl alcohol. When the preparation was made with aniline in dry benzene, the substance was obtained free from solvent, in small, pale yellow needles from xylene, m. p. 279° (Found : C, 78·3; H, 4·6; N, 12·6. $C_{22}H_{15}ON_3$ requires C, 78·3; H, 4·45; N, 12·5%). This substance, or the alcoholate freed from alcohol, did not take up alcohol again on standing for some days over that solvent, nor did it form a hydrate on being left over water.

Pyridinium Bromide Derivative of (XV).—When a solution of (XV) in an excess of pyridine was heated for some hours, reddish-brown needles of (XVI) were gradually deposited. The substance, crystallised from aqueous alcohol and dried over calcium chloride, was obtained as the hygroscopic *monohydrate* (Found : C, 59·7; H, 3·8; Br, 18·5. $C_{21}H_{14}ON_3Br,H_2O$ requires C, 59·7; H, 3·8; Br, 18·9%). After 3 weeks' exposure to air, the stable *trihydrate* was obtained (Found : C, 55·3; H, 4·3; loss at 120°, 11·6. $C_{21}H_{14}ON_3Br,3H_2O$ requires C, 55·0; H, 4·5; H_2O, 11·5%). (XVI) was insoluble in organic solvents, but was extremely soluble in water, giving a solution containing ionised bromine. From water, it formed bright red needles, which darkened near 285° and decomposed with effervescence near 295°. It dissolved in cold aqueous sodium hydroxide to a deep purplish-red solution, which became pale yellow with excess of acid (reversible change).

Action of Bromine on SS'-*Dimethyldithio*-β-iso*indigo*.—The dimethyl derivative was dissolved in boiling chloroform, and excess of bromine added; long, dark red, silky needles of a *dibromide* separated, m. p. 152—154° (after being dried over phosphoric oxide) (Found : C, 45·7; H, 2·9; Br, 33·5. $C_{18}H_{14}N_2Br_2S_2$ requires C, 44·8; H, 2·9; Br, 33·15%). On being boiled with water, the substance decomposed into bromine and the original dimethyl derivative.

Action of Bromine on β-iso*Indigo*.—β-*iso*Indigo (2·5 g.) and bromine (3 c.c.) were heated at 100° in a sealed tube for 4 hours. The yellow viscous mass solidified when boiled with water and was then dried and extracted with hot methyl alcohol. The filtered extract eventually deposited a microcrystalline powder, which became a pale yellow, viscous liquid at about 230° (Found: C, 49·7; H, 2·7; N, 7·05%) and was probably a mixture of the nuclear (6-) mono- and di-bromo-derivatives of β-*iso*indigo. Part of this was repeatedly boiled for a short time with 10% sodium hydroxide solution; from the filtered solution acetic acid precipitated a pale yellow powder (Found : N, 6·6. $C_{16}H_8O_2N_2Br_2$ requires N, 6·7%). This *substance* was probably 6 : 6'-dibromo-β-*iso*indigo. The crude substance, on being oxidised with chromic acid in glacial acetic acid, gave 5-bromophthalimide in colourless prismatic needles, m. p. 230° (Waldman, *J. pr. Chem.*, 1930, **126**, 65).

Synthesis of (I) *from Dithiophthalimide*.—(1) Dithiophthalimide was heated in an oil-bath at 220° for 1 hour and then at 250° for ½ hour. The melt was extracted with carbon disulphide to remove sulphur and a trace of tar; the residue was shown in several ways to be (I) in a nearly pure state. (2) Dithiophthalimide (1 part) was dissolved in warm alcohol (8 parts); the solution was cooled and to it was added aqueous ammonia (*d* 0·88; 4 parts) : (I) soon separated from the intensely red solution, and was freed from sulphur by extraction with carbon disulphide and alcohol; the yield of pure product was about 90%.

Synthesis of (I) *from Thiophthalimidine*.—Thiophthalimidine (1 part) was mixed with powdered sulphur (5 parts) and heated at 120° for 1 hour and then slowly up to 200° (4 hours). The residue, extracted with carbon disulphide and alcohol and then crystallised from nitrobenzene, gave (I), the yield being about 50%.

Dithiophthalimide from o-*Cyanothiobenzamide*.—No reaction took place when (II) was boiled under reflux for 3 hours in dry benzene, with passage of dry ammonia and dry hydrogen sulphide (½ hour) through the liquid. However, when alcohol was added, reaction set in at once and was complete in ½ hour. The benzene was distilled off in steam, and the residue crystallised from aqueous alcohol; (IV) then separated in a pure state.

Action of Hydrogen Chloride on o-*Cyanothiobenzamide*.—When (II) was suspended in boiling dry benzene, and dry hydrogen chloride passed in for 1 hour, the suspended solid (XX) was faintly pink. After being dried over sodium hydroxide, it was completely soluble in cold water to an acid solution which precipitated monothiophthalimide on long standing in the cold or at once on warming.

Action of Ammonia on Monothiophthalimide.—Monothiophthalimide dissolved in aqueous ammonia (*d* 0·88) to a yellow solution which at once began to deposit uniform crystals, hydrogen sulphide being liberated. After 1 hour they were removed and dried in a vacuum over concentrated sulphuric acid; they were then only slightly soluble in boiling benzene, but very soluble in alcohol or in hot water. Recrystallisation from hot water (charcoal) gave colourless needles (XVIII), m. p. 205° (Found : C, 65·8; H, 4·0; N, 19·4. $C_8H_6ON_2$ requires C, 65·7; H, 4·1; N, 19·2%). The *substance* was soluble in warm dilute hydrochloric acid, and phthalimide separated on cooling.

Action of Aniline and Hydrogen Sulphide on Phthalonitrile.—Four distinct substances were isolated from reactions carried out under different conditions : (1) Phthalonitrile (4 g.), aniline (20 c.c.), and alcohol (50 c.c.) were boiled under reflux for 4 hours in a stream of hydrogen sulphide; the solid, when filtered off and washed with boiling alcohol and carbon disulphide, gave a pure specimen of (I) (yield, 1·8 g.). (2) Phthalonitrile (4 g.), aniline (10 c.c.), and xylene (10 c.c.) were vigorously boiled under reflux for 6 hours in a stream of hydrogen sulphide; the mixture was distilled in steam, and the solid residue dried, powdered, and extracted with benzene (60 c.c.) in presence of charcoal; the hot filtered extract deposited (VIII) on cooling (yield, 2 g.). (3) Phthalonitrile (4 g.) and aniline (20 c.c.) were gently boiled under reflux for 6 hours in a stream of hydrogen sulphide; the solid remaining after distillation in steam was crystallised from pyridine and the almost black pyridine double compound was decomposed with boiling alcohol; the product (brown needles, m. p. 306°) was shown to consist of (VII). The reaction did not occur when the aniline and phthalonitrile were first dried by heating in a stream of dry carbon dioxide. (4) Phthalonitrile (4 g.) aniline (10 c.c.), and alcohol (10 c.c.) were gently boiled for 4 hours under an air condenser in a slow stream of hydrogen sulphide, the liquid being allowed to evaporate slowly; the dark paste which remained was dried on porous tile and then extracted with alcohol (100 c.c.). The residue was pure (I); the alcoholic filtrate gave crystals (2·1 g.) of (VI) mixed with a small proportion of (VII); pure (VI) was obtained on further crystallisation from alcohol or pyridine. It is shown in the following paper that the action of hydrogen sulphide on phthalonitrile in the presence of a little aniline takes another direction at a higher temperature, a reaction occurring in which the aniline can be dispensed with.

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