

422. *The Benzoyl Derivatives of Indigotin.*

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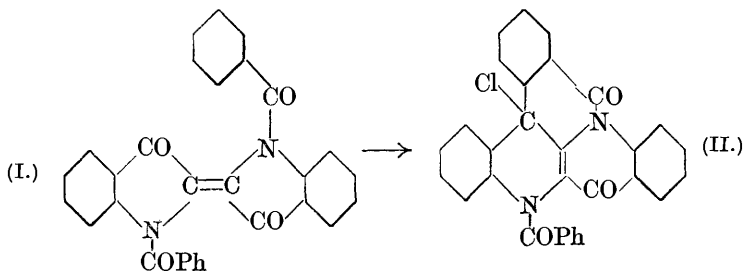
Two of the products of direct benzylation of indigotin under various conditions are described in the literature as *NN'*-dibenzoyl derivatives, and of the other three products, which are not simple benzoyl derivatives (Posner and Hofmeister, *Ber.*, 1926, **59**, 1827; Posner, Zimmermann, and Kautz, *Ber.*, 1929, **62**, 2150), Indigo Yellow Ciba 3G or Ciba Yellow 3G ("Colour Index," No. 1195) is of interest both from its connexion with indigotin and as it is of some technical value as a vat dye.

Since the constitutional formulæ of none of these compounds have been definitely established, the benzoyl derivatives of indigotin have been reinvestigated.

NN'-Dibenzoylindigotin.—The brown amorphous *NN'*-dibenzoylindigotin described by Schwartz (*J. pr. Chem.*, 1863, **91**, 382) was prepared by heating indigotin directly with benzoyl chloride at 180°. Posner and Hofmeister have also described a violet *NN'*-dibenzoylindigotin, obtained by benzylation with benzoyl chloride in pyridine solution, which probably has this constitution, as it gives indigotin again on hydrolysis.

Repetition of the work of Schwartz showed that the supposed brown dibenzoylindigotin could not be a simple benzoyl derivative, as it contained chlorine. It was identical with the substance $C_{30}H_{17}O_3N_2Cl$, known as the "Dessoulayv compound" (D.R.-P. 247154) and obtained by boiling indigotin with benzoyl chloride until the blue colour had disappeared.

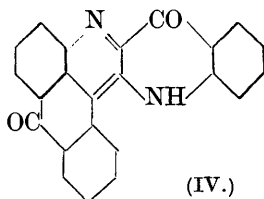
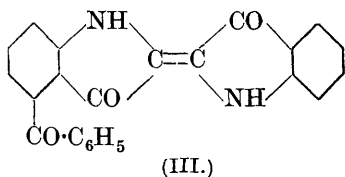
The Dessoulayv compound was also formed from the violet *NN'*-dibenzoylindigotin by the more prolonged action of benzoyl chloride (Posner, Zimmermann, and Kautz, *loc. cit.*).



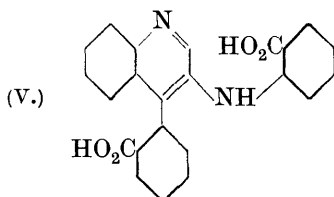
It seems likely that the Dessoulayv compound is formed from *NN'*-dibenzoylindigotin as the result of one of the carbonyl groups of the indigotin structure condensing with the nucleus of the

adjacent benzoyl group. A somewhat analogous reaction occurs in the formation of Lake Red Ciba B by the action of phenylacetyl chloride on indigotin (*Ber.*, 1924, 57, 1311). This reaction, followed by a readjustment of the ring systems and substitution of chlorine for the hydroxyl group, leads to the formula (II) for the Dessoulayv compound. This formula makes clear its relationship both to *NN'*-dibenzoylindigotin and to Ciba Yellow 3G.

Ciba Yellow 3G.—This substance is obtained by the prolonged action of benzoyl chloride on indigotin at 150° in the presence of a catalyst such as copper powder. It has the formula $C_{23}H_{12}O_2N_2$ (Posner and Hofmeister), which corresponds to a monobenzoyl-indigotin less $1H_2O$. Posner and Hofmeister suggested that it is formed by direct substitution of benzoyl into a benzene nucleus of the indigotin molecule, followed by ring closure and a readjustment of the ring systems to give an anthraquinone derivative (IV).



The most characteristic property of *Ciba Yellow 3G* is that on heating with 15 per cent. caustic soda solution it takes up water to form the sodium salt of a carboxylic acid, from which *Ciba Yellow 3G* can be regenerated on warming in neutral solution. Posner and Hofmeister regarded this substance as a dicarboxylic acid (V), their evidence for its dibasic character resting on the analysis and on the formation of a diethyl ester.



A re-examination of the carboxylic acid showed that its properties were not in agreement with Posner and Hofmeister's formulation, and were not consistent with their formula for *Ciba Yellow 3G* itself. It was not as basic as an anthranilic acid derivative of this constitution should be, and it was further shown by electrometric titration to be a monobasic acid.

Posner and Hofmeister's "diethyl ester" loses alcohol on treat-

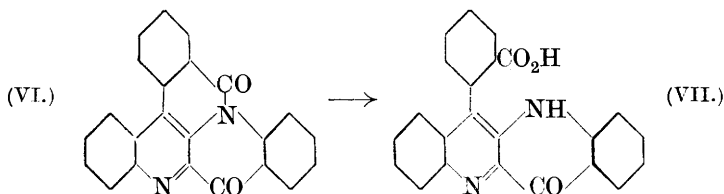
ment with cold dilute sodium carbonate solution, or at 160°; it therefore has not the properties of an ester, and it would appear more probable that the alcohol in it is held only by co-ordination or as "alcohol of crystallisation."

The reversible formation of a carboxylic acid by Ciba Yellow 3G under the conditions described suggested that the relation between these two substances is that of amino-acid to lactam (cf. VI and VII). This was confirmed by methylating the carboxylic acid with methyl sulphate, which gave a *dimethyl* derivative,



in which one methyl group was attached to carboxyl, since it could readily be hydrolysed to give a *monomethyl-carboxylic acid*, $\text{C}_{22}\text{H}_{12}\text{ON}(\text{NMe}\cdot\text{CO}_2\text{H})$, and the remaining methyl group was attached to nitrogen, since it was not removed by heating with hydriodic acid at 140°. In agreement with this view, no ring closure occurred on heating the *N*-methylcarboxylic acid alone or in neutral solution.

The Dessoulayv compound formed Ciba Yellow 3G by the elimination of benzoyl chloride on further heating alone or in the presence of a catalyst. The formula suggested above for the Dessoulayv compound is in consonance with the formula (VI) proposed for Ciba Yellow 3G. Formula (VI) makes clear its relationship to *NN'*-dibenzoylindigotin and to the Dessoulayv compound and is in agreement with all the properties of the substance. It explains the formation of the carboxylic acid (VII) on heating with 15% caustic soda solution, and is further supported by the formation of phthalic acid on oxidation, by the alkali degradation of Ciba Yellow 3G to



give anthranilic acid and a *hydroxy-acid* $\text{C}_{16}\text{H}_{11}\text{O}_3\text{N}$, no doubt *3-hydroxy-4-phenylquinoline-2'-carboxylic acid*, and by further evidence described in the experimental part.

The other complex products formed by the action of benzoylating agents on indigotin are being investigated.

EXPERIMENTAL.

The supposed brown dibenzoylindigotin of Schwartz was prepared by his method (*loc. cit.*), and had all the properties described. It was further boiled in C_6H_6 with charcoal, and on standing for 5 days the solution deposited a

brown semicryst. mass. Recryst. twice from xylene, it formed pale brown crystals containing chlorine, m. p. 238°; yield, 8.5 g. from 15 g. of indigotin. It was identified with the Dessoulayv compound by mixed m. p. determination.

The violet *NN'*-dibenzoylindigotin was prepared by Posner and Hofmeister's method (*loc. cit.*). Yield, 75%; m. p. 254°. When it (1 g.) was boiled with benzoyl chloride (15 g.), the violet colour changed within 5 min. to brown, and crystals of the Dessoulayv compound (1.0 g.) separated on cooling. Recryst. from xylene, this had m. p. 240°; it was identified by mixed m. p.

Ciba Yellow 3G, $C_{23}H_{12}O_2N_2$.—The prepn. given in D.R.-P. 259145 was modified as follows: Indigotin (60 g.), Cu powder (6 g.), and $ZnCl_2$ (30 g.) were heated with benzoyl chloride (130 g.) and nitrobenzene (500 c.c.) for 1½ hr. at 150°. The product was washed with acetone, and the Ciba Yellow 3G separated from a small amount of Höchst R and Höchst U by boiling with 15% NaOH aq. and reprecipitating the Ciba Yellow 3G by warming the filtered neutral solution. Cryst. from xylene, the dye (20 g.) had m. p. 288°.

A Cl-substituted Ciba Yellow 3G was prepared in the same way by means of *m*-chlorobenzoyl chloride; m. p. 306° (Found: C, 72.5; H, 3.2; N, 7.3. $C_{23}H_{11}O_2N_2Cl$ requires C, 72.2; H, 2.9; N, 7.3%).

Relation of Ciba Yellow 3G to the Carboxylic Acid.—Ciba Yellow 3G dissolved in boiling 15% NaOH aq. to give the Na salt of a carboxylic acid, which was obtained as a bright yellow ppt. on acidification. The acid could not be obtained cryst., since it partly lost H_2O to form Ciba Yellow 3G on drying or on attempted crystn.; the analysis, therefore, is not satisfactory evidence for the formula. The acid dissolved slightly with a red colour in 30% HCl but was insol. in dil. acid. The neutral solution of the acid in alkalis deposited Ciba Yellow 3G slowly on standing and quickly at 40°. By electrometric titration with a H electrode, the acid was found to be monobasic; 0.5 g. required 2.3 c.c. $N/2$ -NaOH.

Co-ordination Compounds with Alcohol.—The carboxylic acid (3 g.) was heated for 15 min. at 65° with EtOH (150 c.c.); the filtered solution on cooling deposited pale yellow crystals (2.6 g.). The compound was decomposed by cold dil. Na_2CO_3 aq., in which it dissolved, and the solution gave a ppt. of the bright yellow carboxylic acid on acidification. The compound slowly lost EtOH to form Ciba Yellow 3G on drying at 160° and melted at 286–288°, *i.e.*, the m. p. of this dye (Found: C, 72.2; H, 5.1. $C_{23}H_{14}O_3N_2, C_2H_5OH$ requires C, 72.8; H, 4.9%).

The corresponding compound with MeOH was prepared by warming the carboxylic acid (1 g.) with MeOH (80 c.c.) at 50° (Found: C, 72.5; H, 4.5; N, 6.9. $C_{23}H_{14}O_3N_2, CH_3OH$ requires C, 72.4; H, 4.5; N, 7.0%).

Methylation of the Carboxylic Acid.—The acid (12 g.) was dissolved in 15% NaOH aq. (100 c.c.) and shaken with Me_2SO_4 (30 c.c.) below 35°. The pptd. Na compound was dissolved in dil. Na_2CO_3 aq., and the filtered solution acidified, giving a ppt. of a monomethyl-carboxylic acid (9 g.), yellow needles, m. p. 232°, after recrystn. from EtOH.

Further methylation at 50° gave a *dimethyl* derivative insol. in dil. alkali (*cf. Ber.*, 1926, 59, 1835), which was hydrolysed by dil. NaOH aq. or by HI aq. to give the monomethyl-carboxylic acid (Found: MeO, 7.6. $C_{22}H_{12}ON \cdot NMe \cdot CO_2Me$ requires MeO, 7.8%).

The *monomethyl-carboxylic acid* was slightly basic, since it dissolved to give a red solution in 15% HCl. It was sol. in dil. Na_2CO_3 aq. or dil. NaOH aq., but with 25% NaOH aq. formed an oily Na compound similar to the ψ -indoxyl

derivatives observed by Sidgwick and Plant (J., 1925, **127**, 209) (Found : C, 75.5; H, 4.5. $C_{24}H_{16}O_3N_2$ requires C, 75.8; H, 4.2%).

The methyl-carboxylic acid began to lose CO_2 at 280° ; the *product* was insol. in alkali and formed yellow needles, m. p. 168° from AcOEt (Found : N, 8.2. $C_{23}H_{16}ON_2$ requires N, 8.3%).

Alkali Degradation of Ciba Yellow 3G.—The dye (9 g.) was heated with 10% NaOH aq. (90 c.c.) for 7 hr. at 220° in a steel tube. The colourless crystals which separated on cooling (2.5 g.) were the Na salt of an acid, $C_{16}H_{11}O_3N$, which crystallised from EtOH in colourless rhombs, m. p. 220 — 230° with gas evolution (Found : C, 72.5; H, 4.2; N, 5.2. $C_{16}H_{11}O_3N$ requires C, 72.5; H, 4.1; N, 5.3%).

The acid $C_{16}H_{11}O_3N$ was a *hydroxy-acid*, since when heated alone or warmed in acid solution it formed a *lactone*, which crystallised in pale yellow needles, m. p. 215° , from AcOH, and was sol. in hot 8% NaOH aq. (Found : C, 77.3; H, 4.0; N, 5.8. $C_{16}H_9O_2N$ requires C, 77.7; H, 3.7; N, 5.7%).

Anthranilic acid also was isolated (0.5 g.) and in smaller amounts a yellow pyridone *derivative*, m. p. above 360° after crystn. from cyclohexanone (Found : C, 83.7; H, 3.6; N, 5.8. $C_{17}H_9ON$ requires C, 83.9; H, 3.7; N, 5.8%), and a *substance* isomeric with the lactone described, but having the properties of a lactam and forming colourless needles, m. p. 228° , from AcOH (Found : C, 77.7; H, 3.7; N, 5.7%). By the action of 15% NaOEt on Ciba Yellow 3G there was obtained a *base*, insol. in dil. NaOH aq., which formed colourless needles, m. p. 197° , from AcOH (Found : C, 78.1; H, 3.6. $C_{16}H_{10}ON_2$ requires C, 78.1; H, 4.0%). Of these substances, only anthranilic acid could be identified.

The Dessoulavy Compound, $C_{30}H_{17}O_3N_2Cl$.—This substance was prepared by heating indigotin with benzoyl chloride at 180° (D.R.-P. 247154). The Dessoulavy compound (1 g.), heated in paraffin (30 c.c.) to 315° , decomposed to give benzoyl chloride and Ciba Yellow 3G. Cryst. from xylene, this had m. p. 287° ; it was identified by its solubility in 15% NaOH aq. and by mixed m. p. (cf. D.R.-P. 247155).

Ciba Yellow 3G is also formed from the Dessoulavy compound at a lower temp. in the presence of a catalyst, so that it is probable that the Dessoulavy compound is an intermediate in the technical prepn. of Ciba Yellow 3G. The Dessoulavy compound (1 g.) was heated with $ZnCl_2$ (0.5 g.), Cu powder (0.1 g.), and benzoyl chloride (0.5 c.c.) in nitrobenzene (10 c.c.) for 5 hr. at 150° . The product was a mixture of Ciba Yellow 3G with Höchst U, which was separated by treatment with 15% NaOH aq. The former was identified by mixed m. p.

The authors thank the Gesellschaft für Chemische Industrie (Basle) for certain materials, and the Chemical Society for grants.

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[Received, October 15th, 1932.]