[Contribution from the Chemical Laboratory, Case School of Applied Science]

6,8-DICHLOROBENZOYLENE UREA, AND THE INTERACTION OF 5,7-DIHALOGEN ISATOIC ANHYDRIDES WITH AMMONIA.—A NEW REAGENT FOR SODIUM

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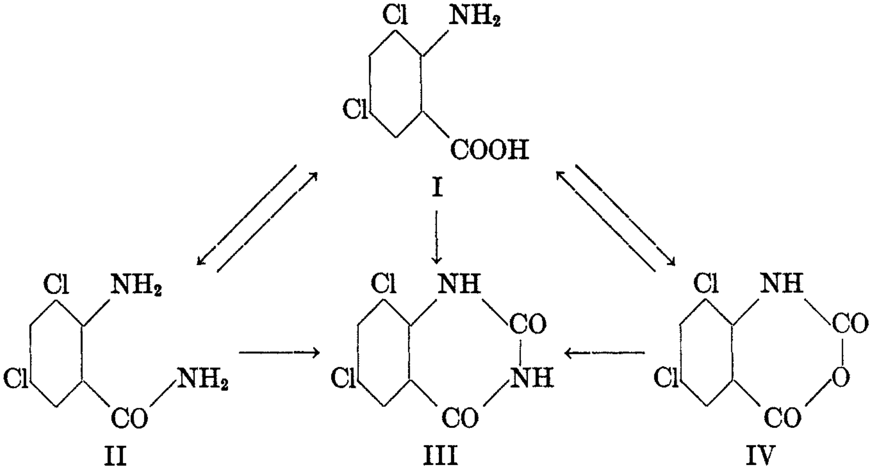
During the course of a series of experiments[1] designed to show the positions of the nitro groups in 6,8-dinitrobenzoyleneurea, it was observed that the key-compound of the demonstration, 6,8-dibromobenzoyleneurea, forms a sodium salt which is sparingly soluble in water and which can be used as a test for sodium in the presence of the other alkali metals. These results suggested that an analogous dichlorobenzoyleneurea might possess similar properties, and an investigation of this point was undertaken.



3,5-Dichloroanthranilic acid (I), like the corresponding dibromo compound,[1] failed to react with aqueous isocyanic acid; on fusing it (I) with urea, however, 6,8-dichlorobenzoyleneurea (III) and appreciable amounts of 3,5-dichloro-2-aminobenzamide (II) were obtained. Attempts to prepare 6,8-dichlorobenzoyleneurea by heating benzoyleneurea with sulfuryl chloride during fourteen hours, and by direct chlorination in

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[1] Sheibley and Turner, *J. Am. Chem. Soc.*, **55**, 4918 (1933).

hot glacial acetic acid solution were unsuccessful, the benzoyleneurea being apparently unchanged. The amide (II) reverts to 3,5-dichloroanthranilic acid (I) on alkaline hydrolysis, and is identical with the 3,5-dichloro-2-aminobenzamide prepared by Franke[2] from *o*-aminobenzamide and sulfuryl chloride. Phenyl isocyanate and benzoic acid are known to react with loss of carbon dioxide to form benzanilide,[3] and it is possible that the dichloro amide (II) produced in the fusion experiments is formed by an analogous splitting of carbon dioxide between dichloroanthranilic acid and isocyanic acid; but according to J. M. Das-Gupta[4] aromatic monobasic acids do not give amides when fused with urea or heated with it in various solvents. 3,5-Dichloroanthranilic acid, therefore, was heated with urea in glacial acetic acid and in glycerol as recommended[5] for aliphatic acids and phthalic anhydride, but the formation of (II) under these conditions was not realized. Benzoyleneurea is sometimes prepared by fusing anthranilic acid with urea, but *o*-aminobenzamide has not been detected in the melt,[6] and hence cannot be considered an intermediate product, despite the fact that it does give benzoyleneurea on fusion with urea.[7] 3,5-Dichloro-2-aminobenzamide (II), fused with urea at 160–165°, gave 6,8-dichlorobenzoyleneurea (III) in 80 per cent. yield; a comparison of this result with the 67 per cent. yield of the same product (III), obtained in a dichloroanthranilic acid fusion conducted at 160–165°, and the 48 per cent. yield from a similar fusion conducted at 140°, indicates that in this case the dichloro amide (II) is probably a partial intermediate. The ready formation of uramino compounds on reaction of aminobenzoic acids and their amides with urea or isocyanic acid is well known, and the ease of conversion of the ortho isomers into benzoylene ureas affords an explanation of these fusion reactions which applies equally well to the direct acid fusions and those in which an intermediate amide may be involved.[4, 6, 8]

6,8-Dichlorobenzoyleneurea (III) is a high-melting substance with properties analogous to those of the 6,8-dibromo derivative.[1] It dissolves in aqueous potassium hydroxide to give solutions which yield a crystalline precipitate with solutions of sodium salts but are not affected by salts of lithium, rubidium, or cesium. 6,8-Dibromobenzoyleneurea requires lithium hydroxide, which tends to absorb atmospheric carbon dioxide and precipitate lithium carbonate, for its solution, and is altogether a less

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[2] Franke, *J. prakt. Chem.*, [2], **44**, 431 (1891).

[3] Dieckmann and Breest, *Ber.*, **39**, 3052 (1906).

[4] Das-Gupta, *J. Indian Chem. Soc.*, **10**, 117, 169 (1933).

[5] Reference 4, pp. 118, 123.

[6] Bogert and Scatchard, *J. Am. Chem. Soc.*, **41**, 2056 (1919).

[7] Abt, *J. prakt. Chem.*, [2], **39**, 141 (1889).

[8] Jacobs and Heidelberger, *J. Am. Chem. Soc.*, **39**, 2437 (1917).

convenient reagent for sodium testing than the dichloro compound. Sodium 6,8-dichlorobenzoyleneurea, precipitated from solutions of the potassium and lithium salts, is a sesquihydrate, in contrast to the previously described sodium 6,8-dibromobenzoyleneurea which is a monohydrate.

In 1886 Robert Dorsch[9] oxidized 5,7-dichloroisatin, prepared by direct chlorination of isatin, with chromic anhydride and obtained 5,7-dichloroisatoic anhydride. This compound he treated with aqueous ammonia and thus arrived at a product which melted at 284° and was assigned the constitution of 3,5-dichloro-2-aminobenzamide. Five years later Franke[2] prepared this amide by the action of sulfuryl chloride on *o*-aminobenzamide; he observed a melting point of 175° and discussed the inconsistency with Dorsch's measurement. Since 5,7-dichloroisatin can be prepared from tetrachloroindigo,[10] and Kolbe[11] obtained isatoic anhydride directly from indigo without isolating the intermediate isatin, 5,7-dichloroisatoic anhydride (IV) was prepared by direct oxidation of tetrachloroindigo with chromic anhydride. The product (IV) possesses the properties described by Dorsch[9] for this compound, and on treatment with ammonium hydroxide yields a substance which melts at 285° and is identical with 6,8-dichlorobenzoyleneurea (III) prepared by the fusion methods. 5,7-Dichloroisatoic anhydride (IV) was also prepared by heating 3,5-dichloroanthranilic acid (I) with ethyl chlorocarbonate, a method which is useful for the preparation of isatoic anhydride.[12] The product (IV), obtained in this manner, is identical with that prepared from tetrachloroindigo and exhibits the same behavior with ammonium hydroxide. By oxidation of tetrabromoindigo the corresponding 5,7-dibromoisatoic anhydride was likewise prepared. Dorsch[13] described this compound and apparently obtained 3,5-dibromo-2-aminobenzamide when he treated it with aqueous ammonia, but in the present experiments 6,8-dibromobenzoyleneurea[1] was produced. A comparison of the melting points recorded by Dorsch[9] for the mono- and dihalogen derivatives of this series indicates that in general the isatoic anhydride has a melting point 30–60° higher than that of the acid, which in turn melts at a temperature approximately 30° above the melting point of the amide. The value of 284° recorded for the dichloro amide is the only anomaly; undoubtedly the product with which this observation was made was 6,8-dichlorobenzoyleneurea (III) and not 3,5-dichloro-2-aminobenzamide (II).

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[9] DORSCH, *J. prakt. Chem.*, [2], **33**, 51 (1886).

[10] GRANDMOUGIN AND SEYDER, *Ber.*, **47**, 2366 (1914); ASINGER *Monatsh.*, **63**, 389 (1933).

[11] KOLBE, *J. prakt. Chem.*, [2], **30**, 87 (1884).

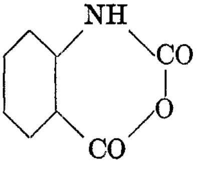
[12] NIEMENTOWSKI AND ROZAŃSKI, *Ber.*, **22**, 1673 (1889).

[13] Reference 9, p. 47.

When 5,7-dichloroisatoic anhydride (IV) is heated with ammonium hydroxide 6,8-dichlorobenzoyleneurea (III) and 3,5-dichloroanthranilic acid (I) are produced in the proportions required by the equation:

$$\underset{\substack{\text{Dichloroisatoic}\\\text{anhydride}}}{5C_8H_3O_3NCl_2} + 2NH_3 + H_2O \rightarrow \underset{\substack{\text{Dichlorobenzoylene}\\\text{urea}}}{2C_8H_4O_2N_2Cl_2} + \underset{\substack{\text{Dichloroanthranilic}\\\text{acid}}}{3C_7H_5O_2NCl_2} + 3CO_2$$

5,7-Dibromoisatoic anhydride behaves in the same manner. Just how this change occurs is not clear; 3,5-dichloro-2-aminobenzamide was not affected by hot aqueous ammonium carbonate, and a mixture of the amide and dichloroisatoic anhydride failed to react when suspended in hot, very dilute sodium hydroxide solution.



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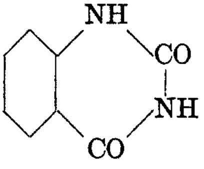

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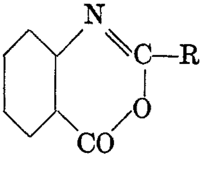

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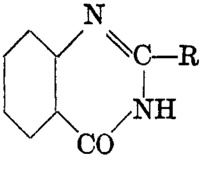

VIII

Isatoic anhydride (V) is a derivative of 3,1,4-benzoxazine, and the ready conversion by ammonia of the alkyl benzoxazones (VII) into the corresponding quinazolones (VIII),[14] sometimes quantitatively, suggests that a quantitative conversion of (V) into benzoyleneurea (VI) on treatment with ammonia would be a normal reaction; and that the actual conversion of (V), under these conditions, into *o*-aminobenzamide[15] is anomalous. The formation of benzoyleneureas by the action of ammonia on isatoic anhydrides has never been reported, although a direct conversion by ammonia of isatoic diazide into benzoyleneurea was observed recently.[16]

EXPERIMENTAL

3,5-Dichloroanthranilic acid (I) was prepared by direct chlorination,[17] and by treating anthranilic acid hydrochloride with sulfuryl chloride.[18] The compound is conveniently crystallized from alcohol, but the recovery is poor, and the material in the mother liquors is not easily reclaimed due to the concentration of impurities. Crystallization from benzene is efficient provided the initial material is not too impure. The crude products recovered from mother liquors were dissolved in dilute ammonium hydroxide, and the solutions were boiled until the ammonia was driven off and dichloroanthranilic acid, suitable for recrystallization purposes, began to crystallize.

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[14] Beilstein, "Handbuch der organischen Chemie," 4th ed., Vol. 27, p. 207.

[15] Kolbe, *J. prakt. Chem.*, [2], **30**, 475 (1884).

[16] Darapsky and Gaudian, *ibid.*, [2], **147**, 51 (1936).

[17] Elion, *Rec. trav. chim.*, **44**, 1106 (1925).

[18] Eller and Klemm, *Ber.*, **55**, 222 (1922).

The pure acid separates from dilute alcohol in sheaves of small white needles, m.p. 233–233.5° (corr.). It is soluble in ether and insoluble in hot water.

6,8-Dichlorobenzoyleneurea (III) from 3,5-Dichloroanthranilic acid (I).—Three grams each of urea and 3,5-dichloroanthranilic acid were mixed and fused in a flask equipped with a loose-fitting cork stopper carrying a vertical exit tube, and placed in an oil bath at 140°. After periods of heating which varied from four to eight hours, the mass was allowed to cool, was powdered, and extracted with 50 cc. of hot 5% aqueous sodium hydroxide solution in order to remove unchanged acid and any high-melting, alkali-soluble materials. The alkali-insoluble residue, consisting of 3,5-dichloro-2-aminobenzamide and sodium 6,8-dichlorobenzoyleneurea, was collected, washed with water, and suspended in hot dilute sulfuric acid. The resulting acid-insoluble mixture of dichloroaminobenzamide and dichlorobenzoyleneurea was in turn collected, washed with water, and extracted successively with three 50-cc. portions of hot 5% potassium hydroxide solution, each extract being subsequently diluted with 50 cc. of water, reheated, allowed to settle, and decanted from the insoluble material before proceeding with the next extraction. The extracts and insoluble material were combined, reheated to dissolve any dichloroaminobenzamide and potassium dichlorobenzoyleneurea which tended to crystallize, and filtered hot from the undissolved residue of crude dichloroaminobenzamide. The clear, colorless to yellow filtrate was acidified with dilute sulfuric acid, and the resulting yellow precipitate was collected, washed, and again extracted with 50 cc. of hot 5% sodium hydroxide. The insoluble residue of sodium salt was removed by filtration, washed with water, and suspended in hot dilute sulfuric acid to give crude dichlorobenzoyleneurea which was collected, washed, and dried. Acidification of the sodium hydroxide filtrate yielded a precipitate of dichloroanthranilic acid, resulting principally from alkaline hydrolysis of the amide.

TABLE I

YIELDS OF CRUDE PRODUCTS FROM FUSIONS OF 3,5-DICHLOROANTHRANILIC ACID AND UREA

TEMPERATURE, °C.	TIME, HOURS	DICHLOROBENZOYLENEUREA, G.	DICHLOROAMINOBENZAMIDE, G.	DICHLOROANTHRANILIC ACID, G.
140	8	0.90	1.21	0.15
140	8[a]	1.63	1.1	0.2
160–165	4	2.25	0.32	0.16

[a] Two heating periods: 5 hours + 3 hours.

The yields of crude products varied considerably with the temperature and duration of heating. Some comparable results are given in Table I.

6,8-Dichlorobenzoyleneurea (III) is sparingly soluble in the usual solvents, 1 g. requiring about 135 cc. of boiling alcohol to dissolve it. It is best crystallized from hot glycol or boiling alcohol, and separates from its solutions in the latter solvent in fine needles, usually of a pale yellow color, m.p. 296° (corr.), after sintering and undergoing an apparent change of crystalline form in the neighborhood of 280°.

Anal. Calc'd for $C_8H_4Cl_2N_2O_2$: C, 41.59; H, 1.75; Cl, 30.69.

Found: C, 41.80; H, 2.07; Cl, 31.11.

The color of this product is apparently due to traces of a yellow impurity, small amounts of which remained as an insoluble residue when the crude dichlorobenzoyleneurea was dissolved in alcohol. This substance sublimes in yellow needles which are not melted at 300°.

3,5-Dichloro-2-aminobenzamide (II).—The crude amide obtained from the fusion preparations was dissolved in hot alcohol, any insoluble residue of the yellow substance described above being removed by filtration. This compound has marked crystallizing power, and separates readily from its alcoholic solutions in white, glistening, prismatic needles, m.p. 182.5° (corr.). On warming with aqueous potassium hydroxide solution for six hours, the amide was slowly hydrolyzed to 3,5-dichloroanthranilic acid, as described by Franke.[2]

A specimen of 3,5-dichloro-2-aminobenzamide, prepared by the action of sulfuryl chloride on *o*-aminobenzamide at room temperature, and crystallized from benzene, following the procedure of Franke,[2] did not alter the melting point of the fusion product already described, and proved to be identical with the latter in all respects.

The white acicular sublimates which invariably deposited on the upper walls of the flasks during the urea-dichloroanthranilic acid fusions were crystallized from hot water, dilute alcohol, or benzene and found to consist of fairly pure dichloroaminobenzamide. The pure amide, however, shows no tendency to sublime when heated.

The solutions of all three of these compounds, the amide, the acid, and the benzoyleneurea, in alcohol and in aqueous caustic alkalies, exhibit a pale bluish-violet fluorescence, enhanced by impurities, in reflected light.

6,8-Dichlorobenzoyleneurea (III) from 3,5-Dichloro-2-aminobenzamide (II).—A mixture of 1 g. of 3,5-dichloro-2-aminobenzamide and 1 g. of urea was placed in the apparatus already described for the dichloroanthranilic acid-urea fusions, and heated at 160–165° during four hours. The melt gradually solidified throughout the heating period, after which it was allowed to cool, was powdered, and extracted with hot solutions of sodium and potassium hydroxides, following the procedure outlined above. A small amount of dichloroanthranilic acid (0.02 g.) was recovered, the usual acicular deposit of sublimed amide being identified by crystallization from hot water and comparison with an authentic specimen. The yield of crude dichlorobenzoyleneurea was about 0.9 g.; it was crystallized from alcohol and did not depress the melting point of a corresponding preparation from the acid.

Anal. Calc'd for $C_8H_4Cl_2N_2O_2$: Cl, 30.69; N, 12.13.
Found: Cl, 30.82; N, 11.84, 12.07.

6,8-Dichlorobenzoyleneurea as a reagent for sodium.—Like its dibromo analog,[19] 6,8-dichlorobenzoyleneurea dissolves in aqueous lithium hydroxide to give solutions which yield white crystalline precipitates with solutions of sodium salts. Unlike the dibromo compound, however, dichlorobenzoyleneurea is readily soluble in warm potassium hydroxide to solutions which crystallize comparatively slowly on standing and are more useful for purposes of sodium testing, since the possibility of lithium carbonate precipitation is eliminated. These solutions are not precipitated by salts of potassium and lithium respectively, and remain clear when solutions of cesium and rubidium chlorides, or mixtures thereof, are added. Mixtures containing sodium chloride give the characteristic precipitate.

A reagent was prepared by dissolving 0.1 g. of potassium hydroxide and 0.05 g. of dichlorobenzoyleneurea in 10 cc. of water, warming, and allowing to cool. Equal volumes of this reagent and known solutions were mixed and observed, precipitation sometimes being incited by rolling the tubes between the hands. Results of comparative precipitation tests are outlined in Table II.

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[19] Reference 1, p. 4921.

With ammonium chloride the reagent instantly gives a white precipitate of dichlorobenzoyleneurea.

Sodium 6,8-Dichlorobenzoyleneurea.—Two-tenths gram of potassium hydroxide and 0.15 g. of dichlorobenzoyleneurea were dissolved in 40 cc. of hot water; the solution was allowed to cool, was filtered, and 25 cc. of 0.5*M* sodium chloride added with stirring. Precipitation began within one-half minute. After standing for one-half hour the precipitate was collected, washed with water, and dried at 40° during two hours. Yield: 0.14 g. of a white micro-crystalline powder.

The yields of the sodium salt were generally equal to the weight of the dichlorobenzoyleneurea taken. Precipitation from hot solutions, and prolonged drying (25 hours) at 40° did not alter the composition of the product. When crude, uncrystallized dichlorobenzoyleneurea was used an impure sodium salt resulted. The analyses were made with five independent preparations of which the first two were precipitated from solutions in lithium hydroxide.

Anal. Calc'd for $C_8H_3Cl_2N_2NaO_2 \cdot 1\frac{1}{2}H_2O$: Na, 8.21. Found: Na, 8.10, 8.22; 8.20, 8.21, 8.20.

Attempts to determine the total water of hydration by extended drying were unsuccessful. At 230° a drying curve finally passed through the theoretical value (9.65% H_2O), but the weight of the sample did not remain constant at this point. At 125° the weight became constant after a loss of 6.45%, a value agreeing closely with the theoretical (6.43%) for two thirds of the total water present, *i.e.*, for 1 H_2O.

TABLE II

PRECIPITATION OF SODIUM WITH 6,8-DICHLOROBENZOYLENEUREA

SALT	MOLARITY	REMARKS
Sodium chloride	0.5	Heavy white precipitate immediately.
Sodium chloride	0.2	Precipitate within ten minutes.
Sodium chloride	0.1	Precipitate within one hour, later becoming voluminous.
Sodium chloride	0.05	Trace of precipitate after four hours or later.
Rubidium chloride	1.0	Behaves like 0.1*M* sodium chloride.
Cesium chloride	1.0	No precipitate.

5,7-Dichloroisatoic anhydride (IV) from 3,5-dichloroanthranilic acid (I).—One gram of 3,5-dichloroanthranilic acid and 3 cc. of ethyl chlorocarbonate were mixed in an acetylating flask and gently refluxed over a small flame during 12–14 hours. The reaction mixture was allowed to cool, diluted with alcohol, and the insoluble, gray, sandy solid (0.8 g.) was removed by filtration, washed with alcohol, and dried. This product is a mixture of dichloroisatoic anhydride and a small amount of an unidentified substance which is soluble in benzene. The material was extracted with about 40 cc. of boiling benzene, and the cold extract was separated from the undissolved residue of dichloroisatoic anhydride by filtration. The residue was dissolved in a boiling mixture of acetone and alcohol (1:1), and the resulting solution was filtered and evaporated on a water bath to incipient crystallization. From solutions prepared in this manner, 5,7-dichloroisatoic anhydride separates in glassy, pale-yellow prisms, m. p. 261° (corr.) with evolution of gas but without darkening of the melt. The compound dissolves easily in warm, dilute sodium hydroxide to solutions which yield precipitates of dichloroanthranilic acid on acidification.

Anal. Calc'd for $C_8H_3Cl_2NO_3$: Cl, 30.56. Found: Cl, 30.58.

The unidentified substance mentioned above separated from its solutions in benzene, amyl alcohol, or acetone-alcohol mixtures in white pasty or chalky masses melting in the neighborhood of 220°. Hot aqueous ammonia or, better, sodium hydroxide dissolved it very slowly; and acidification of the resulting alkaline solutions gave white, highly insoluble precipitates which were not melted at 300°.

5,7-Dichloroisatoic anhydride (IV) from tetrachloroindigo.—Five grams of tetrachloroindigo* was suspended in 50 cc. of glacial acetic acid, and with frequent shaking, 9 g. of chromic anhydride was added in small portions during a period of seven hours. The mixture, kept at room temperature by occasional immersions in an ice bath, was finally packed in a small amount of ice and allowed to stand overnight. It was then heated at 50° during one-half hour and at 70° for another half-hour, was allowed to cool, and was poured into a liter of water which had been acidified with 5 cc. of concentrated sulfuric acid. After standing for four hours the yellow brown precipitate, 2.5 g., which had separated was collected, washed with water, dried, and crystallized from an acetone-alcohol mixture in the manner described above, yielding 1.4 g. of brownish crystals, m. p. 254–255° with foaming, as recorded by Dorsch.[9]

5,7-Dichloroisatoic anhydride thus prepared invariably had a darker color than the product obtained from dichloroanthranilic acid and ethyl chlorocarbonate as outlined above, but mixtures of the two products melted at temperatures identical with the melting points of their components.

5,7-Dibromoisatoic anhydride.—On treating a suspension of 1.5 g. of tetrabromoindigo in 15 cc. of glacial acetic acid with 1.8 g. of chromic anhydride, following the procedure just described for tetrachlorindigo, there was obtained 1.0 g. of an orange brown precipitate which, crystallized from acetone-alcohol, yielded 0.7 g. of small, pale brown prisms,[13] m. p. 263.5° (corr.) with gas evolution, and identical in appearance with dichloroisatoic anhydride except for the color. This oxidation proceeds more slowly than that of the corresponding tetrachloro compound; consequently, for cooling purposes cold water is preferable to an ice bath, and a longer heating period (1 hour) at 70° is necessary.

Interaction of 5,7-dichloroisatoic anhydride (IV) with ammonia: 6,8-dichlorobenzoyleneurea (III).—One-half gram of 5,7-dichloroisatoic anhydride was heated with 20 cc. of ammonium hydroxide (28%) on a water bath during one hour, shaking occasionally. The heavy granular anhydride gradually became voluminous and flocculent. The suspension was allowed to cool and the undissolved material (0.20 g.) was removed by filtration, washed with water, and dried. Acidification of the ammoniacal filtrate produced a precipitate, 0.25 g., of 3,5-dichloroanthranilic acid which was identified by crystallization from benzene and determination of the melting point of a mixture with an authentic specimen.

The ammonia-insoluble material was dissolved in a hot solution of potassium hydroxide, filtered, and precipitated with a solution of sodium chloride. The separated sodium salt, collected, washed, and warmed with dilute hydrochloric acid, left a residue of 6,8-dichlorobenzoyleneurea which melted at 285°† after a crystallization from alcohol. Recrystallization from hot glycol gave small, pale-yellow prisms, m. p. 296° corr., alone or mixed with specimens of the same compound prepared by the two fusion methods already described.

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* Courtesy of General Dyestuff Corporation. New York, N. Y.

† Dorsch, reference 9, p. 53, gives m. p. 284° for his product, which was mistaken for the amide of dichloroanthranilic acid.

In a preliminary experiment performed with a sample of dichloroisatoic anhydride prepared from tetrachloroindigo, the ammonia-insoluble residue of 6,8-dichlorobenzoyleneurea was crystallized directly from acetone-alcohol as described by Dorsch.[9] The product was a gray white mass of minute needles having the correct melting point, and without a suggestion of a yellow color.

When 5,7-dibromoisatoic anhydride was similarly treated with ammonia, results contrary to the experience of Dorsch[20] but corresponding closely with those described above for the dichloro compound were obtained. The ammonia-insoluble portion was crystallized from acetone-alcohol and from glycol and found to be identical (mixture melting point) with 6,8-dibromobenzoyleneurea, m. p. 305–306° (corr.), prepared by the fusion method.[21] The 3,5-dibromoanthranilic acid which precipitated on acidifying the ammoniacal solution was repeatedly crystallized from alcohol, m. p. 235–236° (corr.).[22]

In these experiments the weights of the dihalogen isatoic anhydride taken and those of the corresponding benzoyleneurea and anthranilic acid produced bear to each other the molecular ratios 5:2:3, respectively. The results, calculated on a basis of five moles of the anhydride, are compared in Table III.

TABLE III

REACTIONS OF 5,7-DIHALOGEN ISATOIC ANHYDRIDES WITH AMMONIA

ISATOIC ANHYDRIDE		BENZOYLENEUREA		ANTHRANILIC ACID	
Grams	Moles	Grams	Moles	Grams	Moles
5,7-Dichloro-					
0.50[a]	5	0.20	2.01	0.25	2.82
0.36[b]	5	0.14	1.95	0.17	2.66
5,7-Dibromo-					
0.65	5	0.20	1.54	0.37	3.10
0.33	5	0.13	1.98	0.185	3.05

[a] Prepared from tetrachloroindigo.

[b] Prepared from 3,5-dichloroanthranilic acid. This specimen proved to be slightly impure.

SUMMARY

When 3,5-dichloroanthranilic acid is fused with urea, 6,8-dichlorobenzoyleneurea and 3,5-dichloro-2-aminobenzamide are formed. The amide, fused with urea, likewise gives 6,8-dichlorobenzoyleneurea, and the possibility of its being a partial intermediate in this synthesis is discussed.

6,8-Dichlorobenzoyleneurea, like 6,8-dibromobenzoyleneurea, forms a sodium salt which is sparingly soluble in water and which can be precipi-

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[20] Reference 9, p. 48.

[21] Reference 1, p. 4920.

[22] BOGERT AND HAND, *J. Am. Chem. Soc.*, **25**, 939 (1903), give m. p. 235.5–236° for this acid.

tated in the presence of the other alkali metals. As a test for sodium it is more advantageous than the dibromo compound since it dissolves readily in potassium hydroxide, thus eliminating the use of lithium hydroxide and any precipitation of lithium carbonate by atmospheric carbon dioxide.

5,7-Dichloroisatoic anhydride results on heating 3,5-dichloroanthranilic acid with ethyl chlorocarbonate. Treated with ammonia it yields 6,8-dichlorobenzoyleneurea and 3,5-dichloroanthranilic acid. 5,7-Dibromoisatoic anhydride behaves similarly. These anhydrides were previously reported to give, by this treatment, amides of the corresponding anthranilic acids, a reaction supposedly general for isatoic anhydrides.