330–336° (corr.) (with decomposition), after recrystallization from about 4000 parts of acetic acid. It crystallizes in very fine, yellow needles almost insoluble in xylene, excessively soluble in pyridine.

Subst. (I) 0.2837, (II) 0.5972; cc. 0.1 *N* $AgNO_3$, (I) 15.14, (II) 31.94.
Calc. for $C_{14}H_5O_3NI_4$: I 66.79. Found: (I) 67.73, (II) 67.88.

Tetraiodophthal-*p*-acetylaminoanil.—Fifteen grams of *p*-aminoacetanilide were added to a boiling solution of 50 g. of the anhydride in 200 cc. of nitrobenzene. A part of the product was crystallized from nitrobenzene in minute, yellow blades of melting point 339° (corr.) (with decomposition), unchanged by a recrystallization from nitrobenzene.

Subst. (I) 0.4612, (II) 0.4873; cc. 0.1 *N* $AgNO_3$, (I) 22.79, (II) 24.19.
Calc. for $C_{16}H_8O_3N_2I_4$: I 64.77. Found: (I) 62.72, (II) 63.01.

The product is practically insoluble in xylene and acetic acid, somewhat soluble in phenol and pyridine. One gram dissolves in 400 cc. of boiling nitrobenzene.

Summary.

(1) The systematic study of phthalic acid derivatives from the standpoint of constitution and color has been continued by the preparation of a large number of derivatives of tetrachloro- and tetraiodophthalimides. New methods have been used for the preparation of these compounds which are improvements upon methods previously used for similar preparations.

(2) A study of the action of various amines on nuclear substituted phthalic anhydrides indicates that the first stage of this type of reaction is a molecular addition involving secondary valency forces only, and often resulting in the production of a deep red color. Tertiary amines show no further action on the anhydride ring; primary and secondary amines rapidly break it, forming the colorless amic acid or its salts.

(3) A new type of phthalic acid derivative has been prepared by replacing chlorine in the nucleus by anilino groups.

(4) The dimorphic modifications of tetrachlorophthal-*p*-tolil show a difference in color, melting point, and ability to combine with solvents.

(5) The spectroscopic study of halogenated phthalimide derivatives will be reported in a later paper.

PITTSBURGH, PA.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

PHTHALIC ACID DERIVATIVES; CONSTITUTION AND COLOR, VI. THE ACTION OF AMINES UPON DICHLOROPHTHALIC ANHYDRIDES.

BY DAVID S. PRATT AND GRANVILLE A. PERKINS.

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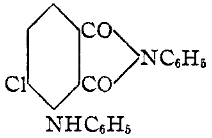
The action of amines on halogenated phthalimides and their derivatives first came to the authors' attention in connection with preparing tetrachlorophthalanil and similar compounds. When the aniline salt of tetrachlorophthalic acid is heated[1] it loses water and aniline, giving the anil. The product, however, is contaminated with deeply colored tarry impurities. Aniline 3,6-dichlorophthalate acts in the same way.[2] The formation of tarry by-products in preparing anils can be minimized by using the method of Tingle and Bates, that is, heating the phthalanilic acid in 50% alcohol; by the method of Graebe and Gourevitz,[3] which consists in heating the anhydride in aniline, or best by the method described in a previous article[4] namely, warming the anhydride with aniline in acetic acid solution. The last is a modification of Zincke & Cooksey's method[5] for phthalanil. For some reason, inexplicable to us, they considered it necessary to keep the temperature down. These three methods, with variations, were found to furnish means for the convenient preparation of a large number of halogenated phthalimide derivatives. This paper, however, deals with some of the tarry by-products mentioned above. We have ascertained that one of the effects of amines upon halogenated phthalimides is to replace one or more halogen atoms. For example the 3,6- and 3,4-dichlorophthalanils on long boiling in aniline give anilinochlorophthalanils. The 3,5-dichlorophthalic anhydride was not available for investigation; from the 4,5-derivative no anilino product was obtained.

Concerning the relative activity of α and β chlorine atoms toward aniline, nothing can be said at present except that the 4,5-dichlorophthalanil is relatively very inactive. This indicates that the α chlorine atom, not the β, in 3,4-dichlorophthalanil is replaced giving 3-anilino-4-chlorophthalanil.



The type of dimorphism existing between the two for ms of 3,4-dichlorophthalanil and of 3-anilino-6-chlorophthalanil has been discussed in connection with tetrachlorophthal-*p*-tolil[6] which exhibits the same peculiarity.

EXPERIMENTAL.

The Dichlorophthalic Acids.

The chlorination of phthalic anhydride was carried on in a similar manner to that described by Villiger[7] but since his manipulation is somewhat

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[1] Graebe and Buenzod, *Ber.*, **32**, 1994 (1899).

[2] Tingle and Bates, THIS JOURNAL, **32**, 1324 (1910).

[3] *Ber.*, **33**, 2024 (1900).

[4] THIS JOURNAL, **40**, 198 (1918).

[5] *Ann.*, **255**, 375 (1889).

[6] THIS JOURNAL, **40**, 208 (1918).

[7] *Ber.*, **42**, 3538 (1909).

difficult when working with large quantities in the laboratory, a simplification was adopted.

Fifteen hundred grams of phthalic anhydride, dissolved in an equal weight of 50% fuming sulfuric acid, were maintained at a temperature of 60–70° while a slow stream of chlorine was passed through for about 40 hours. Since sulfur oxides escaped it was impossible to control the operation by Villiger's method of weighing, and a crude test for sufficient chlorination was resorted to. A small sample was taken and boiled with four times its volume of water. When a few crystals remained undissolved, or when the solution on cooling and seeding with tetrachlorophthalic acid gave crystals within an hour, the chlorination was stopped.

The three dichloro anhydrides formed were separated by Villiger's method. The calcium precipitate weighed 974 g., indicating that 35% of the phthalic anhydride was chlorinated in the 3,6 positions. The zinc salt weighed 1746 g., indicating that 58% of the original anhydride had been changed to the 3,4 and 4,5 derivatives. The yields of pure anhydrides, however, were very poor compared to these figures especially in the case of the 3,4 and 4,5 anhydrides, which are difficult to separate. The melting points of the anhydrides obtained are as follows: (Villiger's figures in parentheses.)

3,4- 120–121° corr. (120–121°); 3,6- 193.5–194.5° corr. (190–191°); 4,5- 187.5–188° corr. (185–187°).

3,4-Dichlorophthalanil.—Forty grams of aniline were added to a boiling solution of 40 g. of 3,4-dichlorophthalic anhydride in 200 cc. of acetic acid. The product, 52 g., represented about 97% yield. This was filtered off after cooling and recrystallized from acetic acid and alcohol. The melting point of 181–181.5° corr. was unchanged by recrystallization from acetic acid. It was analysed by the lime combustion method.

Subst. (I) 0.1732 g., (II) 0.3026 g.; cc. 0.1 *N* $AgNO_3$, (I) 11.94, (II) 20.65.

Calc. for $C_{14}H_7O_2NCl_2$: Cl, 24.28. Found: (I) 24.45, (II) 24.21.

One gram of the anil dissolves in 3 cc. of boiling acetic acid, or nearly 100 cc. of boiling alcohol. It is soluble in ethyl acetate and benzene but does not crystallize as well from the latter.

Dimorphism.—3,4-Dichlorophthalanil usually crystallizes in silky needles with a pale yellow cast. This is the form described above, the melting point of which was taken by the usual method. The usual method, however, does not give the true melting point of this modification, for the powdered substance in the capillary tube changes readily on heating into a different and more stable form. One then observes the melting of this stable form. The true melting point of the needles was found by dipping samples of the fine crystals contained in capillary tubes into a bath at various known temperatures. When dipped into a bath at 172° (corr.) the needles did not melt, but immediately changed to a white powder.

Immersed in a bath at 174° the crystals melted to a pasty condition. Fresh crystals at 178° melted more completely, those on the sides of the tube giving clear droplets which quickly clouded or solidified due to precipitation of the stable form. It is evident that the melting point of the needles is approximately 174° (corr.) but at this temperature fusion is not rapid enough to be complete before precipitation of the stable form sets in.

The stable modification was prepared by allowing the anil to stand several days in contact with acetic acid. The needles disappeared and compact *colorless* prisms were formed that melted at 182–182.5° (corr.). Neither modification contained solvent of crystallization.

3-Anilino-4-chlorophthalanil (4,3,?).—Twenty grams of 3,4-dichlorophthalic anhydride were boiled with 60 g. of aniline for 10 hours in an atmosphere of natural gas. Crystals of aniline hydrochloride were formed on cooling. After mixing with acetic acid the product was poured into dilute hydrochloric acid. The orange precipitate was recrystallized from alcohol using boneblack. Eighteen grams of orange crystals were thus obtained, which on two repetitions of the treatment gave 9 g. with a melting point of 159.5–160° (corr.) unchanged by recrystallization.

Subst. (I) 0.3681 g., (II) 0.4612 g.; cc. 0.1 *N* $AgNO_3$, (I) 10.72, (II) 13.35.
Calc. for $C_{20}H_{13}O_2N_2Cl$: Cl, 10.17. Found: (I) 10.33, (II) 10.26.

One gram of the anilino anil dissolves in 70 cc. of boiling alcohol crystallizing in orange leaflets. It is very soluble in acetic acid.

As an experiment on the further action of aniline, ten grams of 3,4-dichlorophthalic anhydride were boiled gently in aniline for 36 hours. The product was more contaminated by tarry material than before, but 5.5 grams melting at 158–159° were obtained and identified by a mixed melting point with the product from shorter boiling.

3,6-Dichlorophthalanil.—One hundred grams of 3,6-dichlorophthalic anhydride were dissolved in 500 cc. of boiling acetic acid, and 100 g. of aniline added. 110 g. representing an 82% yield, of light yellow blades separated on cooling. After recrystallization from acetic acid, the product had a melting point of 197–8° (corr.), unchanged by boiling with boneblack and recrystallization. Graebe and Gourevitz record a melting point of 191°; Tingle and Bates, 201°. One gram of the anil dissolves in 5 cc. of boiling acetic acid.

Subst. (I) 0.2038, (II) 0.2942; cc. 0.1 *N* $AgNO_3$, (I) 14.05, (II) 20.19.
Calc. for $C_{14}H_7O_2NCl_2$: Cl, 24.28. Found: (I) 24.45, (II) 24.34.

3-Anilino-6-chlorophthalanil.—Twenty grams of 3,6-dichlorophthalic anhydride were boiled with 70 cc. of aniline in an atmosphere of natural gas for about 24 hours. (Short heating was found insufficient.) The product was mixed with acetic acid and poured into dilute hydrochloric acid. The dried precipitate, which weighed 33 g., was recrystallized from acetic acid and twice from alcohol using boneblack. One gram of the substance dissolves in 9 cc. of boiling acetic acid or 110 cc. of boiling alcohol.

Subst. (I) 0.3489 g., (II) 0.4114 g.; cc. 0.1 *N* $AgNO_3$, (I) 10.23, (II) 12.03.
Calc. for $C_{20}H_{13}O_2N_2Cl$: Cl, 10.17. Found: (I) 10.40, (II) 10.37.

Dimorphism.—3-Anilino-6-chlorophthalanil, when crystallized from alcohol was usually obtained in the unstable form of orange needle-like blades, melting at about 141° (corr.) to a clear liquid which quickly solidified. This melting point was determined as in the case of 3,4-dichlorophthalanil. The usual method of slow heating changes the substance to the stable form so that the observed melting point is very close to 160°. Fairly rapid heating, however, causes the powdered crystals to melt or soften at about 141°.

The stable form of small orange prisms may be obtained by letting the blade-like crystals stand in contact with solvent, or by heating them with or without solvent. The change on heating takes place without change in weight, showing that solvent of crystallization is not involved. The prisms melt at 160–160.5° (corr.) Although there was hardly a possibility that the substance could be the same as that obtained from 3,4-dichlorophthalanil, still, in view of the almost identical melting points, the distinction was established by a mixed melting point.

4,5-Dichlorophthalanil.—To a boiling solution of twenty grams of 4,5-dichlorophthalic anhydride in 120 cc. of acetic acid, 20 g. of aniline were added. The product, weighing 22 g., representing 82% yield, was filtered off after cooling and crystallized three times from acetic acid using bone-black. Its melting point of 212.5–213° (corr.) was unchanged by recrystallization.

Subst. (I) 0.3062 g., (II) 0.2714 g.; cc. 0.1 *N* $AgNO_3$, (I) 21.09, (II) 18.76.
Calc. for $C_{14}H_7O_2NCl_2$: Cl, 24.28. Found: (I) 24.42, (II) 24.51.

One gram of the anil dissolves in 15 cc. of boiling acetic acid, from which it crystallizes in colorless rhombic leaflets. Occasionally needles are formed especially from slightly impure solutions. This modification was very unstable and was not further investigated.

Attempts to displace the chlorine by means of aniline were unsuccessful, as the anil was attacked only very slightly on boiling for 48 hours. Extremely long boiling gave nothing but tarry products.

Summary.

(I) The 3,4- and 4,5-dichlorophthalanils have been prepared, and the method applied also in obtaining 3,6-dichlorophthalanil.

(II) The action of boiling aniline on the 3,4- or 3,6-dichlorophthalanils, replaces a chlorine atom by the anilino group, but the 4,5-isomer is relatively inactive.

(III) 3,4-Dichlorophthalanil and 3-anilino-6-chlorophthalanil exhibit dimorphism.

(IV) A study of the spectroscopic relations of the dichlorophthalic acids will be made in the near future.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF PITTSBURGH.]

PHTHALIC ACID DERIVATIVES; CONSTITUTION AND COLOR, VII. DIIODO-, TRIIODO-, AND DICHLORODIIODOPHTHALIC ACIDS.

BY DAVID S. PRATT AND GRANVILLE A. PERKINS.

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The replacement of chlorine in halogenated phthalanils[1] by the anilino group results in a new and interesting type of phthalic acid derivatives, but the reaction is slow and the yields not always good. One of the reasons for preparing the diiodophthalic acids was to experiment on the corresponding replacement of iodine by anilino groups. It was expected that iodine would act more smoothly than chlorine in such a replacement. It was found to act readily enough, but unfortunately tarry products were formed from which no pure substances could be isolated.

The value of the iodophthalic acids as intermediate steps in the preparation of hydroxyphthalic acids will be taken up in connection with establishing their structures, and the spectroscopic relations of these acids to other phthalic derivatives will be discussed in a later paper.

Practically no information could be found in the literature concerning the diiodo, and nothing at all concerning triiodo and dichlorodiiodophthalic acids. Edinger and Goldberg[2] prepared a diiodophthalic acid from 4, iodo-*o*-xylene, and recorded a melting point of 195°, which is about ten degrees lower than what we find for 3,4-diiodophthalic acid, but this is probably the isomer they had.

The partial iodination of phthalic acid was carried out in 50% fuming sulfuric acid, the two methods of treatment employed being long heating at 75°, and rapid heating to 200°. The first gave nearly equal amounts of 3,4- and 3,6-acids, and much smaller amounts of 4,5- and triiodo anhydride. Rapid heating gave the same amount of 4,5- with a larger amount of 3,4- and triiodo anhydride at the expense of the 3,6-. Compared with the action of chlorine on phthalic anhydride,[3] the difference indicated a greater tendency toward the 3,4-positions. The formation of a tri-substitution product was not observed in using chlorine. Although the yield of the 4,5-derivative is small in both chlorination and iodination, it is interesting to note that the only product so far isolated from the mixture obtained by partial bromination is 4,5-dibromophthalic anhydride.[4]

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[1] Cf. two preceding papers.

[2] *Ber.*, **33**, 2880 (1900).

[3] V. Villiger, *Ber.*, **42**, 3530 (1909).

[4] Lesser and Weiss, *Ber.*, **46**, 3937 (1913). But cf. *Ibid.*, p. 3944.