	Theory for $C_6H_3(NO_2)C_2O_2(NHC_6H_4NO_2)_2$.	Found.
Carbon	53.21	53.19
Hydrogen	2.88	2.78

Action of Paranitraniline.—The experiment was carried out in the usual manner. No solid separated from the cold ethereal solution but did when it was allowed to warm to the room temperature. This was purified by the usual process of washing and crystallizing from warm alcohol. Small, warty masses separated. Further crystallization from alcohol gave small, pale yellow needles melting with decomposition at 197°-200°. It was probably a product analogous to those described above. No analysis was made.

Treatment with glacial acetic acid gave fine, yellow needles melting at 248° to 249° with slight decomposition.

The melting-point of 3-nitrophthal-*p*-nitranil obtained by Bogert and Boroschek was 249°.

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THE ACTION OF THE SODIUM SALTS OF DIBASIC ACIDS ON ANILINE HYDROCHLORIDE, AND OF ANILINE ON PHTHALYL CHLORIDE AND SUCCINYL CHLORIDE.

BY FREDERICK L. DUNLAP AND FREDERICK W. CUMMER.

Received March 24, 1903.

IN this Journal,[1] the results of the action of the sodium salts of monobasic acids on the hydrochloride of aniline and of other amines, were reported by one of us. This study has been further extended so as to include the sodium salts of dibasic acids, sodium phthalate and sodium succinate being selected for this experimental work.

When dry sodium phthalate and aniline hydrochloride are heated together, phthalanil is formed, while sodium succinate and aniline hydrochloride produce succinanilide and succinanil. Phthalanil and succinanil are not formed directly from the sodium phthalate or the sodium succinate and the aniline hydrochloride, but they are only the final products, phthalanilide and succinanilide being first formed, then undergoing, at the high temper-

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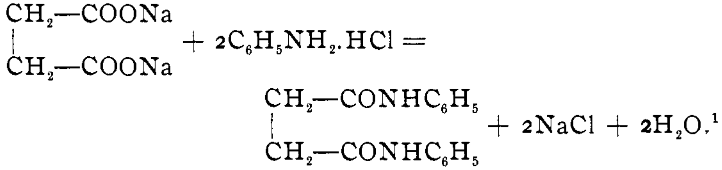
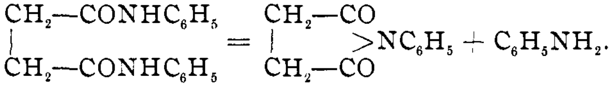
[1] This Journal, **24**, 758 (1902).

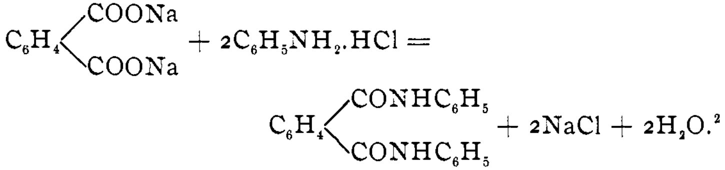
ature at which the reaction is carried out, decomposition into aniline and the corresponding "anil."

1.


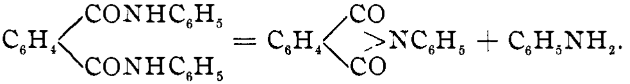
$$\begin{array}{l}CH_2-COONa\\ |\\ CH_2-COONa\end{array} + 2C_6H_5NH_2.HCl = \begin{array}{l}CH_2-CONHC_6H_5\\ |\\ CH_2-CONHC_6H_5\end{array} + 2NaCl + 2H_2O.$$[1]

2.


$$\begin{array}{l}CH_2-CONHC_6H_5\\ |\\ CH_2-CONHC_6H_5\end{array} = \begin{array}{l}CH_2-CO\\ |\\ CH_2-CO\end{array}\!\!>NC_6H_5 + C_6H_5NH_2.$$

3.


$$C_6H_4\!\!\left\langle\begin{array}{l}COONa\\ COONa\end{array}\right. + 2C_6H_5NH_2.HCl = C_6H_4\!\!\left\langle\begin{array}{l}CONHC_6H_5\\ CONHC_6H_5\end{array}\right. + 2NaCl + 2H_2O.$$[2]

4.


$$C_6H_4\!\!\left\langle\begin{array}{l}CONHC_6H_5\\ CONHC_6H_5\end{array}\right. = C_6H_4\!\!\left\langle\begin{array}{l}CO\\ CO\end{array}\right\rangle\!NC_6H_5 + C_6H_5NH_2.$$

In the products of the reaction between the sodium succinate and the aniline hydrochloride, both succinanilide and succinanil were isolated. The higher the temperature, the less the yield of succinanilide obtained. Phthalanilide, at its melting-point, passes readily into phthalanil, with the evolution of aniline vapors. In the case of the sodium phthalate and the aniline hydrochloride, no phthalanilide was isolated, phthalanil alone being obtained. Judging from analogy with the results obtained with the sodium succinate, phthalanilide must be first formed, then undergoing complete decomposition into phthalanil and aniline at a much lower temperature than that necessary for the complete conversion of succinanilide into succinanil and aniline; for at a temperature as low as 130°, the decomposition of phthalanilide is complete, provided this temperature is maintained for a sufficiently long time.

It should be noted that Verley[2] obtained succinimide by distilling a mixture of ammonium chloride and potassium succinate, the succinimide doubtless being produced by the potassium succinate

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[1] It is quite likely that the sodium succinate and the sodium phthalate first form phenylammonium salts, as $\begin{array}{l}CH_2-COONH_3C_6H_5\\ |\\ CH_2-COONH_3C_6H_5\end{array}$ and $C_6H_4\!\!\left\langle\begin{array}{l}COONH_3C_6H_5\\ COONH_3C_6H_5\end{array}\right.$, which, through loss of water, give respectively the phenylamides or anilides, as shown in equations 1 and 3.

[2] *Bull. Soc. Chim.*, [3], 9, 692 (1893).

first forming ammonium succinate, then succinamide, and finally succinimide. At about 200°, succinamide decomposes into succinimide and ammonia.

So far as we have been able to ascertain, phthalanilide was first prepared by van der Meulen,[1] who obtained it by boiling an aqueous solution of the hydrochloride of the iso-methyl ester of phenylphthalamic acid. He found that phthalanilide melted at 251°-252° with decomposition. The year following the appearance of van der Meulen's work, Rogow[2] made a further study of phthalanilide. Rogow states in his paper that phthalanilide had not previously been prepared; but he evidently overlooked the results obtained by van der Meulen. Rogow prepared phthalanilide by the interaction of phthalyl chloride and aniline. He used, as he says, not only a sufficient quantity of aniline to form this compound, but also enough more to combine with the free hydrochloric acid evolved. Rogow used 15 grams of aniline and 5 grams of phthalyl chloride, in which the aniline is in large excess. In this reaction, Rogow used alcohol as a diluent for the aniline, and to this solution, well cooled by salt and ice, the phthalyl chloride was added. The product of this reaction, phthalanilide, he found to have a melting-point of 231°, at which temperature it underwent decomposition. This decomposition, as has been mentioned, is due to the splitting up of this compound into aniline and phthalanil.

In 1901, Kuhara and Fukui[3] reported the results of their study of the action of aromatic amines on phthalyl chloride, at different temperatures. Among the various experiments which they carried out, was one on the action of aniline at ordinary temperatures. This reaction was brought about by allowing phthalyl chloride and aniline, both diluted with ether, to react on one another in the molecular ratio of 1:3 respectively. The only product they mention having obtained, is phthalanil. When, however, this same reaction was carried out at —10°, the product obtained melted at 218°, and, upon analysis, gave results agreeing quite well for phthalanil. Phthalanil melts at 203°: and as the product obtained at the low temperature was capable of being converted into the compound with a melting-point of 203° by heating in a sealed

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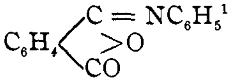
[1] *Rec. trav. chim. Pays-Bas*, **15**, 345 (1896).

[2] *Ber. d. chem. Ges.*, **30**, 1442 (1897).

[3] *Am. Chem. J.*, **26**, 454 (1901).

tube to 140° with *o*-xylol, they called their new product *α*-phenylphthalimide, and assigned it the following structure:



Kuhara and Fukui do not mention Rogow's work, whose results are at direct variance with theirs. Moreover, their methods are practically identical, except that Kuhara and Fukui used ether as a diluent while Rogow dissolved the aniline in alcohol. Kuhara and Fukui also fail to mention the work of van der Meulen,[2] who describes, under the name of phthalphenylisoimide, a compound having the same structure as their *α*-phenylphthalimide, but whose melting-point is 115°-117°.

This question of the products formed from the interaction of phthalyl chloride and aniline, we have resubmitted to experiment. The conditions under which we worked were identical with those of Kuhara and Fukui; namely, with ether as a diluent, at ordinary temperatures and at —10°, as well as with the same reacting masses.

Three products are formed when the reaction is carried on at ordinary temperatures: aniline hydrochloride, phthalanilide, and phthalanil. So far as the phthalanilide is concerned, our results are the same as Rogow's; relative to the phthalanil, our results coincide with those of Kuhara and Fukui. Rogow, however, mentions no product other than phthalanilide, while Kuhara and Fukui mention phthalanil alone. From this we judge that, even if other products were formed, the ones mentioned were the principal products formed.

When ether solutions of phthalyl chloride and aniline react at ordinary temperatures, a heavy white precipitate is formed, consisting of aniline hydrochloride and phthalanilide, while the ether filtrate from this precipitate contains practically no other product except phthalanil, and this in but very small amounts. From

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[1] The experimental portion of this paper referring to the action of phthalyl chloride on aniline was done previous to the appearance of the work of Hoogewerff and Van Dorp (*Rec. trav. chim. Pays-Bas*, **21**, 339 (1902)), excepting the repetition of Kuhara and Fukui's work at low temperatures. The latter was finished previous to the appearance of the review of Hoogewerff and Van Dorp's work in the *Centralblatt*, 1903, I, 156, from which a knowledge of their work was first obtained. We have retained this portion of our experimental work as substantiating the findings of Hoogewerf and Van Dorp relative to the non-formation of α-phenylphthalimide from aniline and phthalyl chloride.

[2] *Rec. trav. chim. Pays-Bas*, **15**, 286 (1896).

these results, it appears that phthalanilide is the main product of the reaction. This experiment has been repeated a number of times, carrying out Kuhara and Fukui's directions as carefully as possible, but always with the results given above.

In carrying out this reaction at low temperatures, Kuhara and Fukui's directions were rigorously adhered to; but we have been unable to substantiate their results so far as the formation of the α-phenylphthalimide is concerned. Kuhara and Fukui treated the reaction product, after filtering off the ether, with water, hydrochloric acid, and ammonia. The residual product they extracted with boiling alcohol a number of times, to remove the phthalanil, after which the remaining product, α-phenylphthalimide, was purified by recrystallization from glacial acetic acid or alcohol, preferably the latter.

The results we obtained show that whatever phthalanil is formed in this reaction, remains in the ether filtrate, and that it is to be found there in only small amounts, mixed with phthalanilide. After treating the main product of this reaction with water, hydrochloric acid, and ammonia, we extracted the residue with boiling alcohol. In all, nineteen extractions had to be made with boiling alcohol before all this residue dissolved. From each one of these alcoholic fractions nothing but phthalanilide separated on cooling, with no trace of any other compound corresponding to α-phenylphthalimide, with a melting-point of 218°.

From the results we have given, it appears that the principal product formed from the interaction of phthalyl chloride and aniline is phthalanilide, while phthalanil occurs in but small amounts, the results being independent of the temperature. Aniline hydrochloride is likewise formed in considerable amounts under both conditions of temperature.

Phthalyl chloride, in a number of its reactions, deports itself as if it had an unsymmetrical structure. For example, with the Friedel and Crafts reaction, it yields diphenylphthalide;[1] on reduction with zinc and hydrochloric acid, phthalide is formed.[2] On the other hand, by reducing with glacial acetic and sodium amalgam, phthalyl chloride yields phthalyl alcohol,[3] a reaction very readily explained by the assumption of a symmetrical struc-

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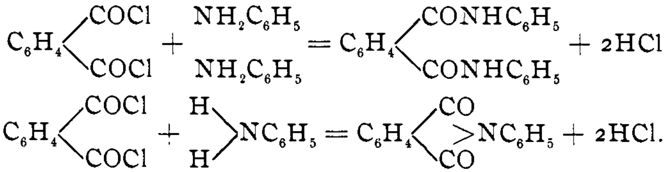
[1] *Ann. chim. phys.*, [6], **1**, 525 (1884).

[2] *Ber. d. chem. Ges.*, **11**, 237 (1875).

[3] *Ber. d. chem. Ges.*, **12**, 646 (1879).

ture for phthalyl chloride. The formation of phthalanilide and phthalanil from phthalyl chloride and aniline, is readily explained by accepting in this case the symmetrical structure for phthalyl chloride.



$$C_6H_4\left<\begin{matrix}COCl\\COCl\end{matrix}\right. + \begin{matrix}NH_2C_6H_5\\NH_2C_6H_5\end{matrix} = C_6H_4\left<\begin{matrix}CONHC_6H_5\\CONHC_6H_5\end{matrix}\right. + 2HCl$$

$$C_6H_4\left<\begin{matrix}COCl\\COCl\end{matrix}\right. + \left.\begin{matrix}H\\H\end{matrix}\right>NC_6H_5 = C_6H_4\left<\begin{matrix}CO\\CO\end{matrix}\right>NC_6H_5 + 2HCl.$$

Or, giving the complete equations, we have for the phthalanilide

$$C_6H_4(COCl)_2 + 4C_6H_5NH_2 = C_6H_4(CONHC_6H_5)_2 + 2C_6H_5NH_2.HCl;$$

while for the phthalanil we have the following:

$$C_6H_4(COCl)_2 + 3C_6H_5NH_2 = C_6H_4(CO)_2NC_6H_5 + 3C_6H_5NH_2.HCl.$$

From these completed equations we can see that, in the first case, we have the phthalyl chloride and the aniline in the molecular ratio of 1:4, while in the second it is only 1:3. We have found in our experiments that, where these compounds were brought together in the ratio of 1:3, the ether filtrate always contained some unchanged phthalyl chloride.

The reaction between succinyl chloride and aniline was also studied, but only at ordinary temperatures. In this case, the products formed were succinanilide and aniline hydrochloride, but no succinanil was isolated. If succinanil is formed in this reaction, it is only in quite small amounts.

In the majority of its reactions, succinyl chloride acts as if it were γ-dichlorbutyrolactone. For example, it passes into butyrolactone on reduction;[1] it reacts with zinc ethyl to produce γ-diethylbutyrolactone;[2] with the Friedel and Crafts reaction it forms γ-diphenylbutyrolactone, but at the same time produces 10 per cent. of symmetrical dibenzoylethane.[3] The fact that symmetrical dibenzoylethane is formed, together with the γ-diphenylbutyrolactone, shows that succinyl chloride deports itself in this reaction like a mixture of the symmetrical and unsymmetrical forms, the latter being predominant. Inasmuch as succinanilide is the sole

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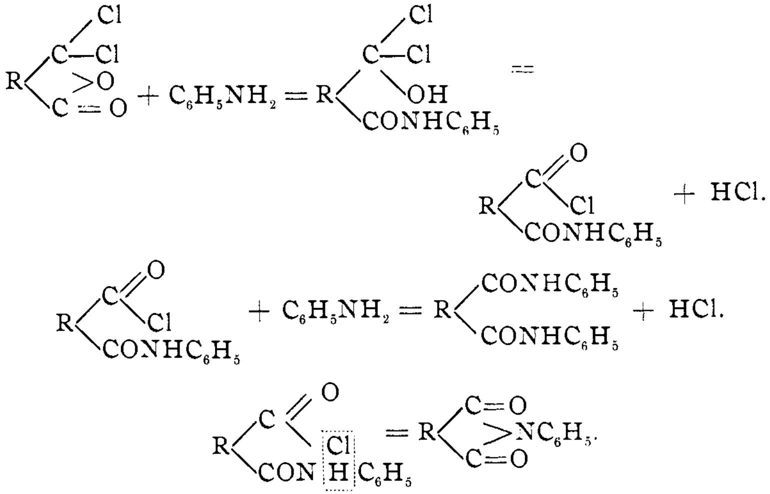
[1] *Ann. Chem.* (Liebig), **171**, 261 (1874); *J. prakt. Chem.*, [2], **25**, 63 (1882).

[2] *Ber. d. chem. Ges.*, **15**, 1851 (1882).

[3] *Ann. chim. phys.*, [6], **22**, 312 (1891).

product of the interaction of succinyl chloride and aniline, we can consider that in this case, as with the phthalyl chloride, the succinyl chloride has a symmetrical structure. These reactions with phthalyl chloride, succinyl chloride, and aniline, can not, however, lead us to any definite conclusions regarding the constitution of these acid chlorides, for the products formed may be explained from a standpoint of an unsymmetrical structure.

For example:



So far as we can see, there is no reason for believing that either phthalanilide or succinanilide have other than the symmetrical structure.

Experimental Part.

ACTION OF SODIUM PHTHALATE ON ANILINE HYDROCHLORIDE.

Dry sodium phthalate and aniline hydrochloride were ground up together in the proportion of one molecular weight of the former to two of the latter. The ground mixture, which developed the odor of aniline quite strongly, was heated in a sealed tube for six hours at 200°. There was no pressure on opening the tube. The solid contents of the tube were ground up several times with water, the water being decanted through a filter. The residue was treated in the same manner with dilute hydrochloric acid, and then given a final washing with water. The product thus obtained was grayish in color. After several washings with small quantities of cold alcohol, the residue was recrystallized from boiling alcohol. The product thus obtained melted at 203°. The melting-point, crystalline form, and solubility in various solvents, were sufficient to identify this product as phthalanil. No phthalanilide was isolated from the products of this reaction; that is, at a temperature considerably below what must be the true melting-point of the phthalanil, this body breaks down into phthalanil and aniline, provided the heating be sufficiently prolonged.[1] From the product obtained by heating sodium phthalate and aniline hydrochloride to only 132° for five hours, no phthalanilide was isolated.

ACTION OF SODIUM SUCCINATE ON ANILINE HYDROCHLORIDE.

Sodium succinate and aniline hydrochloride in the molecular ratio of 1:2 respectively, were ground together and this mixture heated as in the case of the former experiment. The temperature during the heating reached 360°; and while the resulting mass was very dark-colored, both succinanilide and succinanil were obtained from it. A repetition of this experiment, where the heating of the sealed tube was carried on for four hours, and the maximum temperature reached was but 245°, gave a product much lighter in color than in the previous experiment, and yielded the same reaction products. There was a considerable amount of free aniline formed. The contents of this second tube, after washing with cold water and dilute hydrochloric acid, was extracted with boiling water. On cooling, this aqueous extract separated a large amount of slightly colored crystals. Recrystallization from hot water and treatment with bone-black gave a perfectly white product which crystallized in long needle-like crystals, having a melting-point of 150°.

The portion of the original product that was insoluble in water, was dissolved in boiling alcohol and treated with bone-black. This solution, on cooling, separated a crystalline product, which was further purified by several recrystallizations from alcohol. This product had a melting-point of 226°.

The compound with a melting-point of 150° gave 8.29 per cent. N. Calculated for $C_{10}H_9O_2N$, 8 per cent.

The product soluble in water was thus identified by its melting-

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[1] For a discussion of the melting-point of phthalanilide, see the experimental portion of this paper on the action of phthalyl chloride on aniline.

point, and by analysis, as succinanil, while the substance obtained from the alcohol, which had a melting-point of 226°, proved to be succinanilide, and on analysis gave 10.7 per cent. N. Calculated for $C_{16}H_{16}O_2N_2$, 10.44 per cent.

In the experiment in which the mixture of sodium succinate and aniline hydrochloride were heated to 245°, 15 grams of the former substance and 24 grams of the latter were used. From the resulting product, 11.6 grams of succinanil and 3.3 grams of succinanilide were obtained. The higher the temperature at which this reaction is carried out, the larger the relative yield of succinanil.

ACTION OF PHTHALYL CHLORIDE ON ANILINE.

Freshly distilled phthalyl chloride and aniline (in the ratio of one molecular weight of the former to three of the latter) were each dissolved separately in about 300 cc. of ether which had been carefully dried over sodium wire. The aniline solution was slowly added, with constant stirring, to the ether solution of the phthalyl chloride, both solutions being at room temperatures. The reaction caused hardly any perceptible rise in temperature. The addition of the aniline solution produced a heavy white precipitate, which was filtered, washed with ether, and then dried. The ether filtrate, on standing over night, deposited crystals which were filtered off and purified by crystallization from alcohol. These crystals proved to be phthalanilide. The ether filtrate from these phthalanilide crystals, which had deposited on standing over night, was evaporated to dryness and the residue purified by crystallization from alcohol. This product had a melting-point of 203°, and analysis gave results showing that this product was phthalanil. The phthalanilide which separated from the ether solution, had no well-defined melting-point. According to the rapidity of heating, the melting-point could be varied from 20° to 25°, the product always melting with gas evolution (aniline). In its behavior in a melting-point tube, phthalanilide behaves very much like phthalic acid, of which substance no well-defined melting-point can be had, on account of the ease with which it breaks down into phthalic anhydride and water. If the temperature of 225° be held for some time, phthalanilide will finally melt with gas evolution; but, with the ordinary rapidity with which melting-points are taken, the melting-point of phthalanilide usually obtained by us lay some-where between 240° and 250°, while occasionally the melting-point would run still higher. This variable melting-point is doubtless due to the production of more or less phthalanil (m. p. 203°) at a temperature below the true melting-point of the phthalanilide, which phthalanil, as soon as formed, lowers the melting-point of the whole mass.

The white precipitate obtained by the action of the aniline on the phthalyl chloride was, after drying, treated with hot water to remove the aniline hydrochloride. The residue was recrystallized from boiling alcohol, in which, however, it is not very soluble. The only product obtained was phthalanilide. Three analyses were made of this phthalanilide, the per cents. of nitrogen found being 9.11, 9.08, and 9.11, instead of 8.86 per cent. as calculated.

ACTION OF SUCCINYL CHLORIDE ON ANILINE.

In this experiment, freshly distilled succinyl chloride and aniline, both diluted with dry ether, were allowed to interact at ordinary temperatures. An excess of aniline a little greater than the molecular ratio of one of succinyl chloride to three of aniline, was found necessary in order to completely decompose the succinyl chloride. More heat seemed to be developed by this reaction than in the case where phthalyl chloride was used. In fact, if the ether solution of the aniline was added too fast to the ether solution of the succinyl chloride, sufficient heat was developed to cause the solution to boil. The heavy white precipitate produced, was filtered, washed with ether, and dried. Then after thoroughly washing with water, in order to free the product from aniline hydrochloride, the residue was purified by crystallization from alcohol. The pure product had a melting-point of 226.5°, and on analysis proved to be succinanilide. Found, 10.53 per cent. N. Calculated, 10.45 per cent.

The ether filtrate was evaporated to dryness, and an oily product, smelling strongly of aniline, was obtained, showing that an excess of aniline had been used in the reaction. This residue was, however, small in amount. On standing for some time *in vacuo* over sulphuric acid, this oily product became of a pasty consistency. No succinanil was obtained from this residue. If succinanil is formed by the interaction of succinyl chloride and aniline under the conditions we used, it is only in quite small amounts.

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March 1, 1903.