

SOME HALOGEN DERIVATIVES OF ANILINE AND THE EFFECT OF THE
HALOGEN ON THE COLOR PRODUCED BY COUPLING THE
DERIVATIVES TO ALPHA-NAPHTHOL.

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I N T R O D U C T I O N .

The purpose of this research has been to prepare numerous halogen derivatives of aniline, couple these products to alpha-naphthol and note how the position of the halogen in the benzene ring affected the color produced. The experimental work fell naturally into four distinct divisions, i.e., (1) the preparation of the halogen derivative of aniline, (2) the coupling of the aniline derivative to alpha-naphthol, (3) the coloring of white samples of wool, silk and cotton, and, (4) the quantitative analysis of the compound.

The original intention was to prepare twelve aniline derivatives including the ortho, meta, para and 2-4-di-halogen compounds of chlorine, bromine and iodine, respectively. However, only five products were completed before enlistment in the Army forced the author to abandon the research. The fourth division of quantitative analysis was not reached on these five products, so the chart of colored samples at the end of this monograph gives the basis for the conclusions drawn. An effort has been made to present the various steps of preparation in as logical an order as possible and to give the directions in as clear a manner as possible in order that, if the opportunity is presented, the problem may be completed.

For the valuable suggestions throughout this research work the author is indebted to Doctor F. B. Dains under whose guidance the work was undertaken. For this guidance the author wishes to express his sincere appreciation.

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COLOR RESULTS

PREPARATION METHODS.

[Faint, mostly illegible text follows, appearing to be a list of procedures or a detailed description of methods.]

PREPARATION OF 2-4-di-chlor-aniline.

Proportions:-

50 gr. Acetanilide.
750 gr. Acetic Acid (Glacial).
500 gr. Bleaching Powder.
200 cc. Sulphuric Acid.

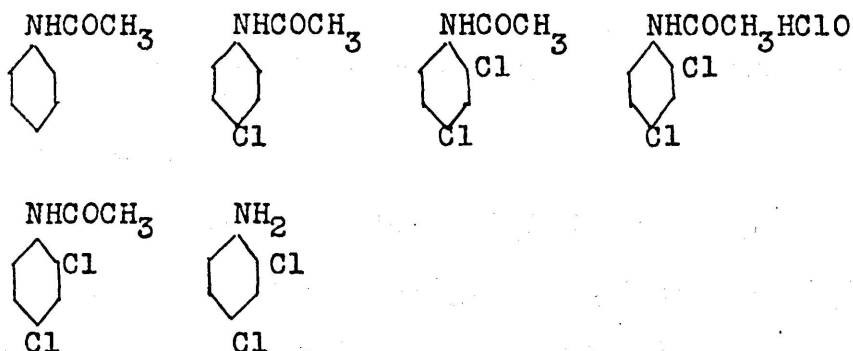
Process:

The acetanilide was dissolved in from 15 - 20 times its weight of dilute acetic acid and the solution heated to about 80° in a porcelain dish. Though the exact amount of acid is immaterial, it is best to have an excess present. Bleaching powder rubbed to a thick cream with water was slowly added, the mixture being constantly stirred, when 1 : 4 chloracetanilide separated. As more bleaching powder was added the 1-2-4-di-chloracetanilide formed. As the cream of bleaching powder was added to the hot, pulpy mass, each addition caused a frothing which kept the mass stirred. The end of the reaction was shown by the free evolution of chlorine, very little having escaped up to this point. The mixture was allowed to stand an hour to settle and cool and then the liquid was decanted while still tepid from the heavy oily additive product. This was a heavy, yellowish oil of a peculiar odor which, on standing, decomposed, depositing crystals of 1-2-4-di-chlor-acetanilide. The replacement of the acetyl group by hydrogen was brought about

by H_2SO_4 . The drained crystals were dissolved in 4 times their weight of H_2SO_4 in a porcelain dish and heated to 115° for 20 minutes. After cooling a little, this solution was poured into an excess of water containing ice, when dichloraniline separated as a white pulp.

Melting Point - Theory, 63° - Found, 60° .

Steps in the Process:-



Reference: Journal of the Chemical Society, Vol. 69, p. 849.

Preparation of 2-4-di-Brom-Aniline.

Proportions:

79.92 gr. Bromine.
67.5 gr. Acetanilide.
82 gr. Sodium Acetate.

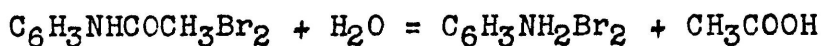
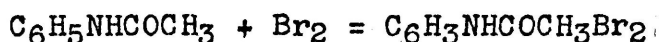
Process:

The sodium acetate was fused to drive off all water then pulverized and thoroughly mixed with the acetanilide. A paste was made of this by mixing it with glacial acetic acid. The bromine was dissolved in an excess of glacial acetic acid and the acetanilide paste slowly added with stirring. This

was gently heated on a water-bath, using a reflux condenser until all bromine color had disappeared. The mixture was now diluted with water when 2-4-dibromacetanilide separated and was filtered off. The dibromaniline was obtained by dissolving the dibromacetanilide in alcohol to which about 1/8 of its bulk of HCl was added. This was boiled 9 hours, the C₂H₅OH distilled off, an excess of NaOH added and the crystallized aniline collected.

Melting Point - Theory, 79° - Found 78°.

Steps in the process:-



Reference: Journal of the Chem. Soc. Jan., 1916.
(See 6a)

Preparation of Ortho-Brom-Aniline.

Proportions:

20 gr.	Bromobenzene.	
15 cc.	HNO ₃	7.1 gr. HCl
15 cc.	H ₂ SO ₄	
19 gr.	SnCl ₂	

Process:-

In order to obtain the ortho-brom-aniline, ortho and para-brom-nitro-benzene were first prepared as follows: A dozen beakers were filled with 15 cc. of HNO₃ and 15 cc. of H₂SO₄ set in ice water and allowed to cool. To each beaker's

Preparation of 2-4-Di-Iodo-Aniline.

Proportions:

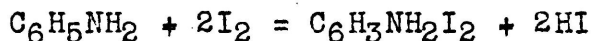
10.8 gr. Aniline.
60. gr. Iodine
25. gr. CaCO₃
60. cc. Ether
60. cc. Water

Process:

The iodine was dissolved in the ether and the CaCO₃ in the H₂O. These were then mixed thoroughly in a 1000 cc. flask and the aniline added. This flask was connected to a reflux condenser, placed in a water bath and boiled until all color due to the iodine had disappeared which required about 16 hours. The ether was now evaporated and the di-iodo-aniline distilled with steam.

Melting Point - Theory, 95° , Found 93°.

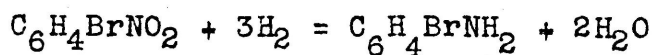
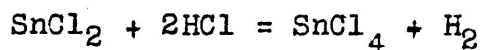
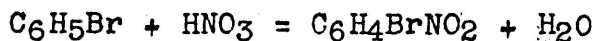
Steps in the Process:



mixture of acid 20 gr. of bromobenzene were added, a very little at a time, with constant stirring. Throughout this reaction care was taken to slow down the reaction by working with small quantities and by keeping the mixtures cool. The ortho and para-brom-nitro-benzene resulted which, after being washed free of acids, was dissolved in 50 % C₂H₅OH. The ortho modification dissolved, leaving the para as a white solid. Upon evaporation of the alcohol, the ortho product crystallized out. This was now dissolved in alcohol and HCl. with SnCl₂ which reduced the nitro-brom-benzene to the ortho-brom-aniline.

Melting Point - Theory, 31° - Found, 29°.

Steps of the process:-



Reference: Cohen Theoretical Organic Chemistry, p. 411.

Preparation of Meta-Brom-Aniline.

Proportions:-

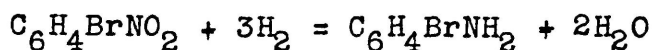
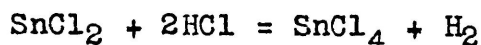
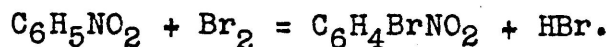
30 gr. Nitrobenzene.
3 gr. Iron wire.
60 gr. Bromine.

Process:

The metabromnitrobenzene was first prepared by placing 30 gr. of nitrobenzene and 3 gr. of iron wire in a flask with reversed condenser and heating up to 120° in an oil-bath. The bromine was then added, one drop at a time, the operation requiring about an hour. The flask was left in the bath and the heating continued until no bromine vapor was visible. The flask was now removed from the bath and the meta-brom-nitro-benzene distilled with steam. After this product had been separated from the water, which came over with it, it was dissolved in alcohol to which was added HCl to give a strong acid reaction. Sannous chloride was now added to reduce the nitro group to the NH₂ and, after making alkaline with KOH, the meta-brom-aniline was obtained by steam distillation.

Melting Point - Theory, 18° - Found, 17.5°.

Steps in the Process:-



Reference: American Chemical Journal, Vol. 19, 1897, p.366.

Preparation of Para-Chlor-Aniline.

Proportions:

25 gr. Acetanilide.
 50 gr. Acetic Acid (Glacial)
 50 gr. Alcohol.
 500 gr. Bleaching Powder.

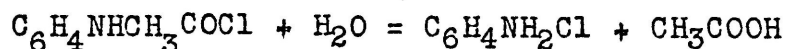
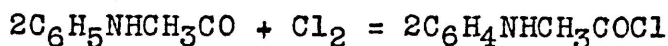
Process:

The acetanilide was dissolved with gentle warming in a mixture of 50 gr. of glacial acetic acid and 50 gr. of alcohol. The solution was then diluted with 500 Cc. of water and heated to 50°. At this temperature a cold 10 % solution of bleaching powder in water was added with continual stirring until 500 Cc. had been added. The para-chlor-acetanilide was collected and washed. For each gram of the acetanilide one gr. of KOH was dissolved in 10 gr. of alcohol. This was poured over the acetanilide and the whole boiled under the reflux for 8 hours. The alcohol was distilled off and the para-chlor-aniline distilled with steam.

Melting Point - Theory, 70° - Found, 69°.

Reference: Barnett's Preparation of Organic Compounds, p. 61.

Steps in the Process:-



Preparation of Para-Brom-Aniline.

Proportions:

5 gr. Acetanilide.
 25 cc. Acetic acid (Glacial).
 6 gr. Bromine.

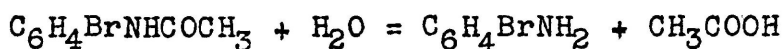
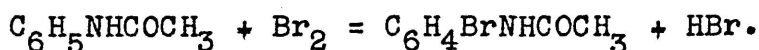
Process:

The acetanilide was dissolved in the acetic acid in a $\frac{1}{2}$ liter flask, the bromine slowly added (dissolved in twice its volume of glacial acetic acid) and the whole well shaken. The mixture was allowed to stand $\frac{1}{4}$ hour and then poured into 200 cc. water. The crystalline precipitate was filtered off and washed 3 or 4 times with water. This precipitate was dissolved in 100 cc. conc. H_2SO_4 , heated to 115° for 20 minutes, and poured into an ice cold beaker of water. The resulting para-brom-aniline was filtered off, washed and dried.

Melting Point - Theory, 63° - Found, 61° .

Reference: Practical Organic Chemistry, Julius B. Cohen, p. 152.

Steps in the Process:-



Preparation of Para-Iodo-Aniline.

Proportions:

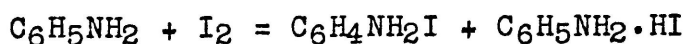
22.4 gr. aniline	60 cc. Ether
30.5 gr. Iodine	60 cc. Water
25. gr. CaCO ₃	

Process:

The iodine was dissolved in the ether and the CaCO₃ in H₂O. These were then mixed thoroughly in a 1000 cc flask and the aniline added. This flask was connected to a reflux condenser, placed in a water bath and boiled until all the color due to the iodine had left, which required 12 hours. The ether was evaporated and the p-iodo-aniline distilled with steam.

Melting Point - Theory, 60° - Found, 58°.

Steps in the Process:-



C O U P L I N G M E T H O D S

Coupling 2-4-di-chlor-aniline To Alpha Naphthol.

Proportions:-

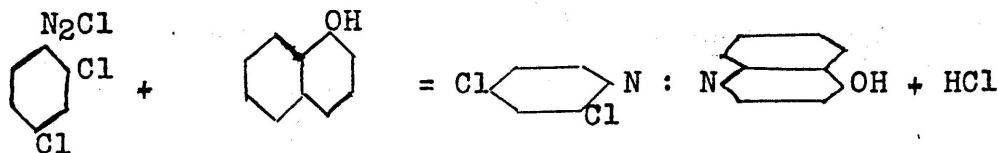
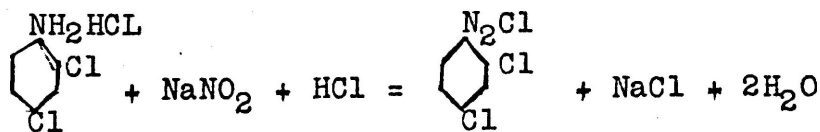
20 gr. 2-4-di-chlor-aniline.
 7 gr. Sodium Nitrite.
 14.6 Alpha Naphthol
 2.9 cc HCl (sp.gr. 1.25).

Process:-

The 2-4-di-chlor-aniline hydrochloride was dissolved in 50 cc of water, cooled to 3° C., the sodium nitrite added and well stirred and then the hydrochloric acid added with constant stirring. This solution was slowly added to an alkaline solution of α naphthol in 50 % alcohol with vigorous stirring. The mixture was allowed to stand until the reaction was complete, when the solid dye was filtered off and dried.

Reference: The Synthetic Dyestuffs. J.C. Cain, p. 49.

Steps in the Process:-



Coupling 2-4-Di-Brom-Aniline To Alpha-Naphthol.

Proportions:

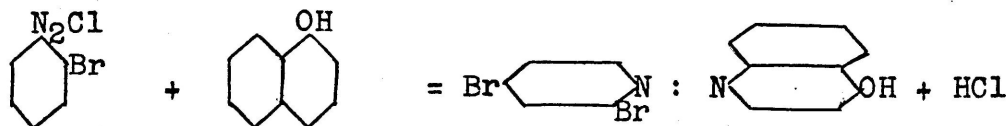
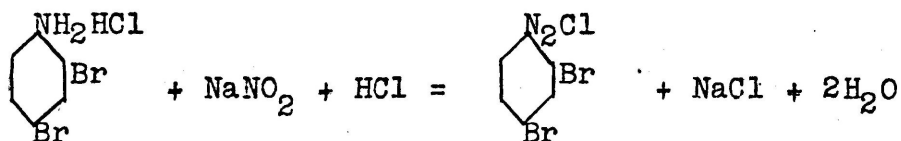
20 gr. 2-4-di-brom-aniline hydrochloride.
 4.8 gr. Sodium nitrite.
 10.1 gr. Naphthol.
 2 cc. HCl (sp. gr. 1.25).

Process:

The di-brom-aniline-hydrochloride was dissolved in 50 cc. of water, cooled to 3° C. in an ice and salt solution and then the sodium nitrite added. The whole was thoroughly stirred and HCl was added. This diazotized solution was poured slowly into an alkaline solution of naphthol in 50 % alcohol, during constant stirring. The mixture was set aside for a day when the solid dye was filtered off and dried.

Reference: The Synthetic Dyestuffs and Intermediate Products, J. C. Cain, p. 49.

Steps in the Process:



Coupling 2-4-di-Iodo-Aniline To Alpha-Naphthol.

Proportions:

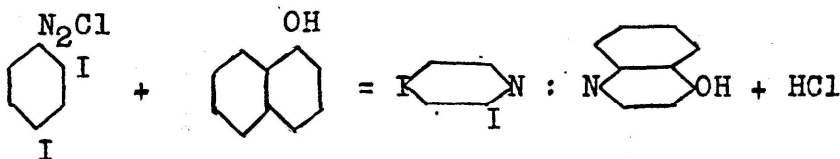
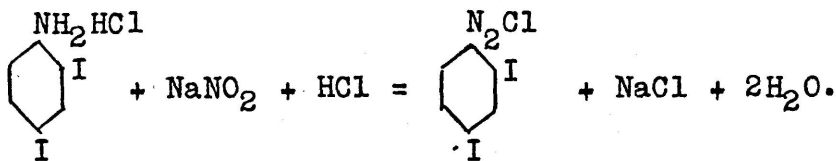
10 gr. 2-4-di-iodo-aniline hydrochloride.
 1.82 gr. Sodium Nitrite.
 .76 cc. HCl (sp.gr. 1.25).
 .38 gr. α Naphthol.

Process:

The 2-4-di-iodo-aniline hydrochloride was dissolved in 50 cc. of water, the sodium nitrite added, the solution stirred and the hydrochloric acid added. This operation was carried out with the temperature near 3° C. The solution thus made was allowed to drop slowly into an alkaline solution of α naphthol. After standing a day, the solid dye was filtered off and dried.

Reference: The Synthetic Dyestuffs. S. C. Cain, p. 49.

Steps in the Process:-



Coupling Para-Chlor-Aniline To Alpha-Naphthol.

Proportions:

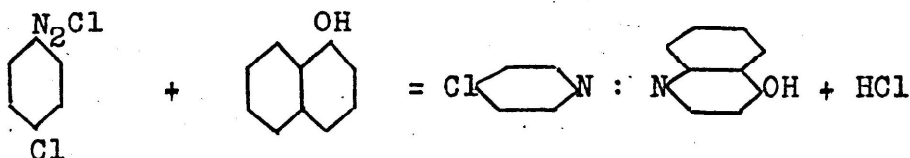
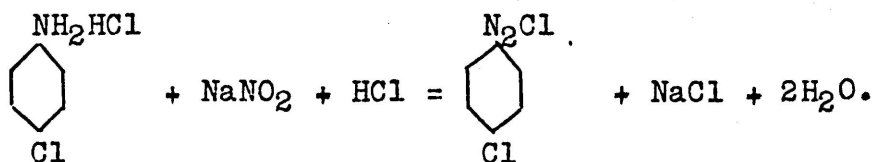
10. gr. Para-chlor-aniline-hydrochloride.
 4.2 gr. Sodium nitrite.
 1.7 cc. HCl (sp.gr. 1.25)
 8.8 gr. α Naphthol.

Process:

The p-chlor-aniline hydrochloride was dissolved in 50 cc. of water, the sodium nitrite added, and the hydrochloric acid added during constant stirring. All the solutions used were cooled to 3° C. This solution was allowed to drop slowly into an alkaline solution of α naphthol and after standing a day the solid dye was filtered off and dried. In order to precipitate the dye more completely NH_4OH was added.

Reference: The Synthetic Dyestuffs. J. C. Cain.

Steps in the Process:



Coupling Para-Brom-Aniline To Alpha-Naphthol.

Proportions:

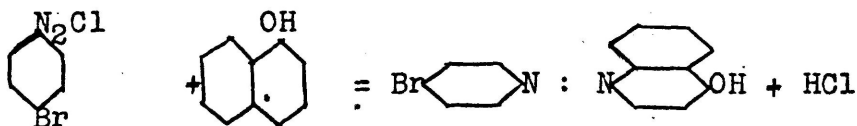
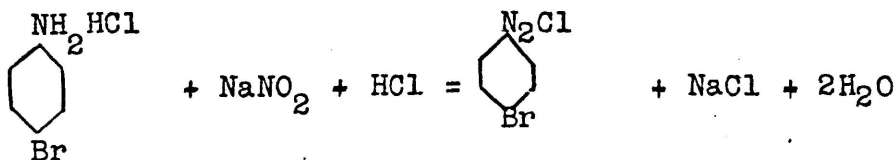
10 gr. p-brom-aniline hydrochloride.
 3.3 gr. Sodium Nitrite.
 1.3 cc. HCl (sp. gr. 1.25).
 6.9 gr. α Naphthol.

Process:

The p-brom-aniline-hydrochloride having been dissolved in 50 cc. of water, the sodium nitrite was added and the temperature reduced to 3°. The HCl was added and this solution allowed to drop into an alkaline solution of α naphthol. The dye settled out after standing a day.

Reference: The Synthetic Dyestuffs. J. C. Cain.

Steps in the Process:



C O L O R R E S U L T S.

In coloring the samples of silk, wool and cotton, the dried dye was dissolved in water, heated to boiling and the strips of cloth dropped in. The boiling was continued ten minutes, the samples removed, rinsed and dried. Care was taken in this operation to use distilled water so that the true effect of mordants could be noted.

In the chart which follows samples number 1, 2,3,4,5, and 6 were all produced by the 2-4-di-chlor-aniline product; samples 7,8,9,10,11 and 12 by the 2-4-di-brom-aniline product; samples 13, 14, 15, 16, 17 and 18 by the 2-4-di-iodo; numbers 19 - 24 by the p-chlor-aniline, and 25 - 30 by the p-brom-aniline. Samples 1, 7, 13, 19 and 25 are silk and upon these the color seemed to be fast to all washing. Samples 2, 8, 14, 20 and 26 are wool and there was no trouble in making the color fast on these strips. However, samples 3, 9, 15, 21 and 27 show cotton without a mordant and show that the dyes would not hold. In specimens 3 and 9 almost all the dye was washed out and in 15, 21 and 27 much was washed out but, due to the darker color, that which remained gave a darker shade than in the other cases. Samples 4, 10, 16, 22 and 28 are cotton and were treated with a boiling solution of tartar emetic before being dyed. It can be noted that there is little difference between this column and that without the mordant, showing that this is

not a suitable mordant. Samples 5, 11, 17, 23 and 29 are cotton having been treated with a boiling solution of tannic acid before being dyed. This mordant evidently held the dye better than the tartar emetic. Samples 6, 12, 18, 24 and 30 were treated with tannic acid, then with tartar emetic before being dyed. The results of these mordants are not satisfactory and, if time permitted, other mordants would have been tried. Of the three, however, the mixture seems to hold the dye best judging from the silk samples as a standard.

In glancing over the chart, especially from top to bottom, it is noted that the lighter colors appear near the top, viz.- di-cl is a light yellow, di-br a darker yellow, and the di-iodo changes over to a red tinge. The p-cl row starts with a light red and the p-br a deep orange. These facts appear not only on the chart but were noted when the dyes were precipitated and in the powder form.

CONCLUSION.

From the observations made, it seems plausible to arrange the dyes according to the ascending molecular weights of the halogens used and by so doing it is found that the color deepens as the molecular weight increases. This rule was proved as far as the work was carried. Reasoning from this, then, the p-iodo product would produce a very dark color as compared to the p-cl and p-br products. As to the relation between the di-halogen and the mono-halogen

colors, the mono seem to be darker though the work was not carried far enough to make this a rule. In conclusion it may be said that the halogens can be arranged according to their ascending molecular weight and the color resulting will vary directly from light to dark.

Chart Showing the Color Produced on Silk, Wool and Cotton
by the Various Dyes Made.

	1 silk	2 Wool	3 cotton No Mordant	4 cotton Tartar Emetic Mordant	5 cotton Tannic Acid Mordant	6 cotton Tartar Emetic and Tannic Acid Mordant
DL-Cl	1	2	3	4	5	6
DL-Br	7	8	9	10	11	12
DL-I	13	14	15	16	17	18
P-Cl	19	20	21	22	23	24
P-Br	25	26	27	28	29	30