THE EFFECT OF BROMINE ON THE SCHIFF BASES

by

Richard W. Blue,
A. B., University of Kansas, 1927

Submitted to the Department of Chemistry and the Faculty of the Graduate School of the University of Kansas in partial fulfillment of the requirements for the degree of Master of Arts.

Approved by:

J B Bains
Instructor in Charge

June 1929

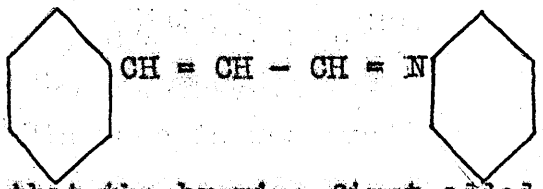
H. P. Cady
Chairman of Department

This page is reserved for the expression of sincere appreciation for the valuable assistance of Dr. F. B. Dains in directing this work, and for the helpful suggestions given by Dr. R. Q. Brewster.

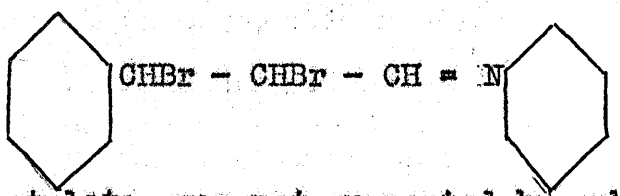
Table of Contents

INTRODUCTION

Schiff,[1] who first studied the addition of bromine to condensation products of aromatic aldehydes and amines of the general type, R-CH=N-R', worked with cinnamic aldehyde anil,



He assumed that the bromine first added to the double bond in the cinnamic aldehyde side-chain, thus:



This postulate was not supported by subsequent investigation, however, as it was found that in general the bromine was eventually substituted in the amine ring rather than in the aldehyde ring; and, in the specific case of cinnamic aldehyde anil, cinnamic aldehyde and para brom aniline were obtained on hydrolysis.

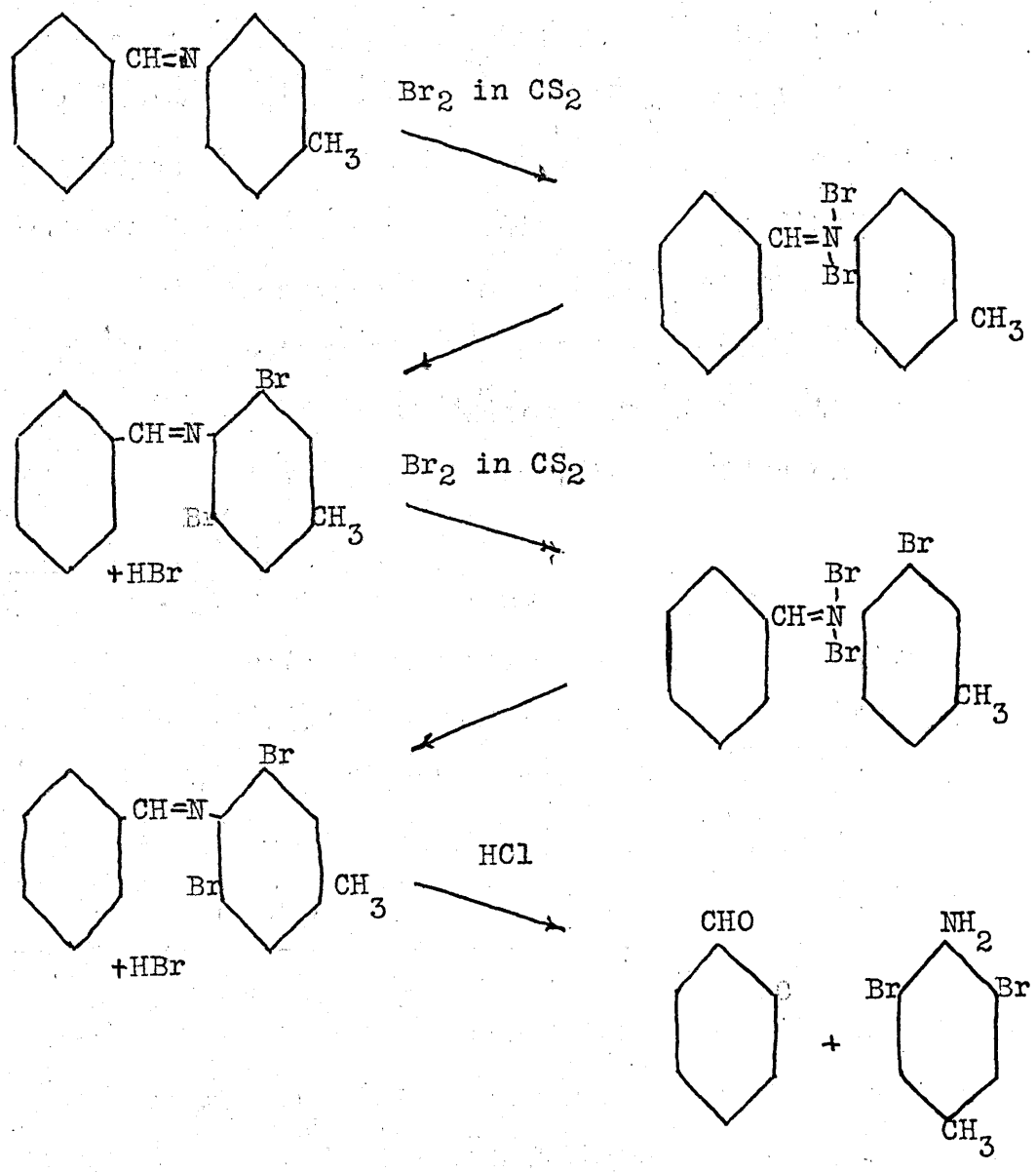
Franzen and his associates[2] explained the effect of bromine by assuming that the bromine first saturated the double bond between nitrogen and carbon.

However, they obtained 1:6 di brom beta naphthyl amine from the hydrolysis of benzylidene beta naphthyl amine di-bromide, the latter product being readily hydrolyzed by boiling in alcohol. The ease of hydrolysis and the substitution of the bromine in the amine ring exclusively are more easily and satisfactorily explained on the basis of the pentavalent nitrogen theory. This theory was first advocated by Hantzsch[3] who assumed that the bromine adds first to the nitrogen and then rearranges. This theory will easily account for the unstable dibromine and the behavior of the bromides on hydrolysis.

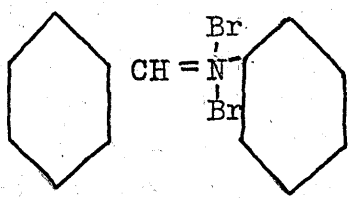
M. A. Berg[5] found that many of the brominated Schiff bases were often very sensitive to water and easily hydrolyzed and that they do not always give consistent results for the determination of bromine, facts which favor the pentavalent nitrogen theory.

Wainscott and Dains investigated the bromination of Schiff bases in order to obtain further evidence on the manner in which the bromine first added to the bases before rearrangement. (Wainscott, Master's Thesis, 1924). The results

indicated strongly the following information which is similar to that suggested by Hantsch[3] and later by James and Judd.[4]



The findings of Wainscott and Dains may be summarized briefly as follows: The first product obtained from the addition of two moles of bromine to a Schiff base is an unstable tri-bromide such as the following:



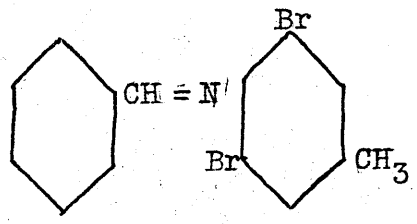
While this cannot be conclusively proved, the formulae given are the only feasible explanation of the facts:

a. That analysis of the brominated base before hydrolysis consistently indicated that three atoms of bromine in the compound;

b. That the brominated bases were in every case readily hydrolyzed;

c. That no brominated aldehyde was obtained from the hydrolysis of any brominated Schiff base; and

d. That compounds of the following type were prepared from the brominated Schiff bases by treatment with pyridine and alcohol:



It was desired to investigate further the addition of bromine to Schiff bases prepared from substituted anilines with particular emphasis on the constitution of the brominated anilines obtained. The chloro and nitro anilines were used in making the Schiff bases for this purpose. At the outset, however, two bases prepared by Wainscott, benzylidene-alpha naphthyl amine and benzylidene-beta naphthyl amine, were studied, as some of the products previously obtained were not crystalline.

EXPERIMENTAL PART

Benzylidene-Beta Naphthyl Amine:-

Fifty grams of beta naphthyl amine were mixed with thirty grams of freshly distilled benzaldehyde and heated on the water bath for an hour. The liquid was poured into water and immediately solidified into a very hard cake. This was broken up in the mortar, washed with dilute alcohol and a dilute acetic acid and dried. The melting point of this product was found to be 95°. The melting point given in literature is 102-3°.[6] Fifty grams of the benzylidene beta naphthyl amine were brominated by Wainscott's method, i.e., by dissolving in dry carbon disulfide (1 gram in 10 c.c.) and adding two moles of bromine (1 gram in 10 c.c.) drop by drop in the cold. The product was filtered from the carbon disulfide and found to be a flocculent yellow solid which gave off a great deal of HBr and some bromine vapor. It darkened rapidly on standing and yielded a tarry mass when treated with water. Two attempts were made to hydrolyze this product by steam distillation in the presence of acid (100 c.c. of water and 15 c.c. of conc. HCl); but the residue left in the distillation flask was a tarry mass. The

tar was filtered off and the cooled filtrate was made alkaline, but only a very small quantity of precipitate was obtained. This melted at 100-104°. One attempt was made using $CaCO_3$ (powdered) instead of acid, but the results were not improved. Also the tar was extracted by boiling repeatedly with dilute acid and making the filtrate alkaline, but only very small quantities of solid were obtained, probably due to the very weak basic properties of the brominated beta-naphthyl amine. Finally, it was found that the brominated Schiff base was not decomposed by treatment with cold 95% alcohol and the hydrolysis was carried out by the following method.

Fifty grams of the brominated Schiff base were thrown into 300 c.c. of alcohol and 25 c.c. of acid were added. The solution was refluxed, with frequent shaking, on the water bath for two hours and allowed to stand over night. The product was filtered off from the cold alcoholic solution, washed with dilute HCl, dilute NaOH, and $NaHSO_3$ solution, and dried. After recrystallization from dilute alcohol, it was found to melt at 121.5°. The melting point given

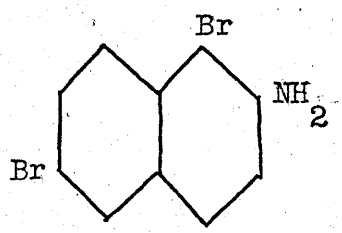
in the literature for 1:6 di-brom beta-naphthyl amine is 121°. Analysis for nitrogen by the Kjeldahl method gave the following results:

Nitrogen found	4.62%
Nitrogen calculated for $C_{10}H_7NBr_2$	4.65%

Some of the product was boiled with acetic anhydride and acetic acid and poured into water. After recrystallization from water the melting point was found to be 208-9°. The melting point of 1:6 di-brom beta acet-naphthalide is 208°. In order to check the constitution of the di-brom beta naphtyl amine several attempts were made to oxidize it to a phthallic acid. The oxidizing agents used were potassium permanganate, chromic acid in glacial acetic acid, and dilute nitric acid (repeated evaporation on the water bath) but in no case was a product obtained which was soluble in alkali and insoluble in cold acid. It was, therefore, determined to synthesize the 1:6 di-brom beta naphthyl amine by direct bromination. The method of Claus and Philipson was used.[8] Aceto beta naphthylide was dissolved in chloroform and bromine in chloroform solution was added, both solutions being cold. The

product was filtered off and crystallized from alcohol. The melting point was found to be 209-10°. Some of this product was then mixed with some of the aceto derivative of the di-brom beta-naphthyl amine derived from the Schiff base and the mixed melting point was found to be 208-9°.

This evidence indicates clearly that the amine obtained from the Schiff base is:



Benzylidene-Alpha Naphthyl Amine:-

Technical alpha naphthyl amine and freshly distilled benzaldehyde were heated for two hours on the water bath, as in the case of beta-naphthyl amine, and poured into water. The product was an oil, all efforts to cause crystallization being unavailing. The oil was dissolved in carbon disulfide and brominated as usual. The product was dried and hydrolyzed in alcohol as with the beta naphthyl amine; but only a very small yield of the

dibrom alpha naphthyl amine was obtained. It was washed and recrystallized and the melting point was found to be 114°. However, the yield was not sufficient to permit the synthesis of the acetyl derivative.

In the attempt to find a relatively high melting Schiff base containing alpha naphthyl amine, piperonal alpha naphthyl amine was prepared and found to yield a very satisfactory product by the following simple process: Equal weights of piperonal and alpha naphthyl amine were dissolved in hot alcohol and mixed. The solution was allowed to stand over night and a large quantity of yellow crystals separated. After drying these were found to melt at 110-111°. Analysis for nitrogen gave the following results:

Nitrogen found	5.26%
Nitrogen calculated for $C_{19}H_{12}ON$	5.16%

No reference to this compound could be found in the literature.

The product was brominated with two moles of bromine and hydrolyzed as in the case of beta naphthyl amine and the giving a good yield of dibrom alpha naphthyl amine. A little was

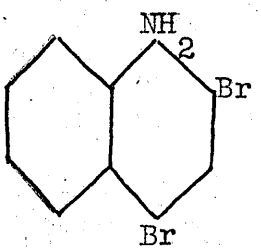
recrystallized twice from 50% alcohol and dried in a dessicator. It was found to melt at 115-16°. The melting point given in literature for 2-4 dibrom alpha naphthyl amine is 118-19°[9]. Analysis for nitrogen gave the following results:

Nitrogen found 4.02% 4.02%

Nitrogen calculated for $C_{10}H_7NBr_2$ 4.65%

Some of the product was acetylated and recrystallized from dilute alcohol. The melting point was found to be 221-222°. The melting point given in literature for the corresponding acetnaphthylide is 225°.

The amine obtained from the Schiff base was, therefore, considered to be:



Benzylidene Para Amino Phenol:

Forty five grams of para amino phenol and forty five grams of benzaldehyde were dissolved separately in alcohol and heated to boiling. They were then mixed and set aside for several hours. The para benzalamino phenol crystallized out and

was filtered, dried, and ground in a mortar. The melting point was 182-6°. That given in literature is 183°. [11] The product was brominated in the usual way except that the CS_2 solution was turbinated better and brominated quite slowly. The precipitate was a dark yellow-green and of good quantity. It was filtered and laid out on filter papers but, since it immediately began to discolor, it was not completely dried but was placed in alcohol at once (300 c.c.) with 50 c.c. of concentrated HCl. The mixture was refluxed for two hours on the water bath and distilled with steam. A very volatile fraction came over first; the distillate then clouded when benzaldehyde began to distill over. When the distillate again became clear, indicating that all benzaldehyde had been removed, the distillation was stopped and the contents of the flask were evaporated nearly to dryness on the water bath. The precipitate of dibrom para amino phenol hydrochloride was filtered off and dissolved in the minimum quantity of fresh water. (A tarry mass which separated at the beginning of the evaporation was removed and immediately became hard and brittle.) It was ground up and submitted to the same treatment as the other

precipitate. The solution was neutralized with sodium carbonate solution and a flocculent precipitate separated out. This was filtered and dried. After boiling with charcoal, filtering, cooling, and again filtering the precipitate was dried and a light brown product was obtained. Several attempts such as this were made to obtain a sample suitable for a melting point determination, but no satisfactory results were obtained, the melting points being low and indefinite. Results were not improved by several attempts to crystallize from benzene.

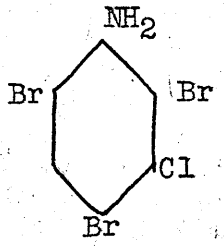
Benzylidene Meta Chlor Aniline:-

Twelve grams of meta chlor aniline were mixed with ten grams of freshly distilled benzaldehyde and the solution was heated for six hours on an oil bath at 110-120°. The product was poured out into a small distilling flask and connected with the Bruhl apparatus. The fraction distilling off at 245-250° at 10 cms. was used for bromination. The boiling point of benzylidene meta chlor aniline at atmospheric pressure is 338°. The Schiff base was brominated as usual in carbon disulphide with two

moles of bromine. The product was placed in the steam still with 100 c.c. of water and 25 c.c. of concentrated HCl and distilled until no more benzaldehyde distilled over. The residue in the flask then consisted of two layers, the water layer and a small viscous layer containing the amine. The upper layer was decanted off and allowed to cool; a considerable quantity of crystalline solid was precipitated. This was filtered off and the filtrate was returned to the steam distillation flask and boiled with the residue. This process was repeated until all of the lower layer dissolved. (The lower layer solidified on cooling but melted again when heated with the boiling dilute acid.) The precipitate which was filtered off in this process was recrystallized from alcohol and found to melt at 124°. The melting point of 2:4:6 tri-brom, 3 chlor aniline is 123.5°.[12] This product was analyzed for nitrogen by the Kjeldahl method with the following results:

Nitrogen found:	3.7%	3.67%
Nitrogen calculated for $C_6H_3Br_3ClN$	3.83%	

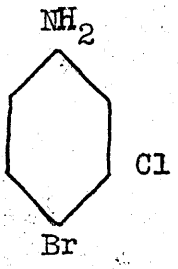
This product was therefore considered to be:



The filtrate from the above operation was made alkaline with sodium hydroxide and yielded 3 or 4 grams of a light colored solid which, when recrystallized from dilute alcohol, yielded bright, light green crystals melting at 67°. The melting point of 3 chlor 4 brom aniline is 67-8°.[13] Analysis for nitrogen gave the following results:

Nitrogen found	7.0%
Nitrogen calculated for C_6H_5NClBr	6.8%

The compound is evidently the mono brom derivative of meta chlor aniline.



Benzylidene Ortho Chlor Aniline:-

The Schiff base was made up in the same manner as was benzylidene meta chlor aniline. The fraction

distilling over at 185-187° at 2-3 cms. was used for bromination. The boiling point of this product is not given in the literature. The analysis of nitrogen gave the following:

Nitrogen found	5.8%
Nitrogen calculated for $C_{13}H_{10}NCl$	6.5%

The brominated product was treated as was the brominated benzylidene meta chlor aniline and four fractions were obtained:

(1) not soluble in boiling dilute HCl;
(2) soluble in hot acid but not incold;
(3) soluble in cold acid but precipitated by alkali, and
(4) distillate.

After recrystallization from alcohol (1) and (2) melted at 101°. The melting point given in the literature for 2 chlor 4:6 di brom aniline is 95°. The distillate also melted at 101° as did the product obtained by hydrolysis in pyridine as shown below. Since the latter product gave accurate results on analysis, the melting point obtained is probably more accurate than the one given in the literature.[12]

After purification (3) melted at 74°. The melting points given in the literature for 2 chlor 4 brom aniline are 70°.[14]

Some of the brominated benzylidene orthochlor aniline was dissolved in pyridine containing a little alcohol and allowed to stand in a stoppered flask for several days. This solution was then poured out into water and, after standing for a week, fine white crystals separated out. The liquor was decanted off and the crystals were recrystallized from alcohol. They melted at 101° and gave the following results on analysis for nitrogen:

Nitrogen found	4.92%
Nitrogen calculated for $C_6H_4NClBr_2$	4.90%

This product was evidently the 2-4 brominated aniline and not the unbroken Schiff base which was expected.

Benzylidene Para Nitro Aniline:-

The Schiff base was prepared as in the case of the chloro derivatives. It was washed with ether and brominated in the usual manner. Three products were obtained after hydrolysis:

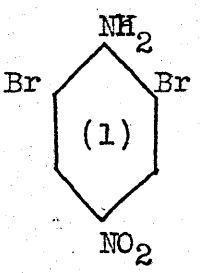
(1) insoluble in hot dilute acid;

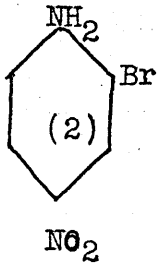
(2) soluble in hot acid but not in cold; and

(3) soluble in cold acid but precipitated

by alkali.

(3) was only a trace. After recrystallization from alcohol (1) melted at 202-4°. The melting point given in the literature for 2:6 di brom 5 nitro aniline is 204°.[16] (2) melted at 107°. The melting point of 2 brom 4 nitro aniline is 104.5°.[17] The products were, therefore, identified as follows:





Benzylidene Para Xylidine:

Twenty grams of 2:5 dimethyl aniline and twenty grams of benzaldehyde were heated on the oil bath for eight hours at 110-20°. The product solidified on being poured into water and was broken up and recrystallized from alcohol. The melting point was 98-100°. The melting point given in the literature for benzylidene para xylidine is 101-2°.[18]

The Schiff base was brominated in chloroform, it having been discovered that bromination in carbon

disulphide yielded a tarry product. The brominated base did not separate from the chloroform immediately as other brominated bases did from carbon disulfide, but after addition of gasoline an oil separated out. This was separated with a separating funnel and hydrolyzed by steam distillation with dilute acid. (After standing for an hour a solid was precipitated from the chloroform and solid continued precipitating from the filtrate after this had been filtered off, giving a very good yield of the brominated Schiff base. This was treated in the same manner as the oil with identical results. The residue in the flask after hydrolysis of the oil was found to be somewhat soluble in hot dilute acid. The undissolved solid residue was filtered off and the filtrate was cooled. Fine white crystals separated from the filtrate and these were dried and found to melt at 65°. The melting point given in the literature for 4:6 di brom 2:5 dimethyl aniline is 65°.[19] As no considerable precipitate was obtained by the addition of alkali, the principal product of the bromination was identified as:

Benzylidene 2:5 Dichlor Aniline:

Thirty two grams of 2:5 dichlor aniline were mixed with twenty grams of benzaldehyde and heated on the oil bath for five hours and then poured out into water. The product immediately solidified and was ground in a mortar. It was washed with dilute alcohol and 30% acetic acid and the melting point was found to be 97°. (No reference could be found to this Schiff base in the literature.)

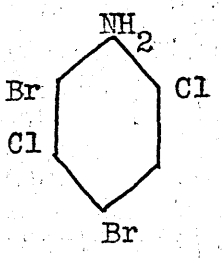
Analysis for nitrogen gave the following results:

Nitrogen found	5.57%	5.5%
Nitrogen calculated for $C_{13}H_9HCl_2$	5.6 %	

The product was brominated in carbon disulfide and hydrolyzed by steam distillation with 15% HCl. Only one product was obtained. It was very slightly soluble in hot dilute HCl. It solidified on cooling and was filtered off and recrystallized from 95% alcohol. The melting point was 108°. The melting point given in the literature for 2:5 dichlor 4:6 dibrom aniline is 108°.[20] Analysis for nitrogen gave the following:

Nitrogen found	4.23%	4.38%
Nitrogen calculated for $C_6H_3NCl_2Br_2$	4.37%	

The product was, therefore, identified as:



Salicylidene Aniline:

Twelve grams of salicylaldehyde were heated with nine grams of aniline on the oil bath at 110° for four hours. The product solidified on being poured into water. It was washed with dilute alcohol and dilute acetic acid and brominated in carbon disulfide. The melting point of the Schiff base was found to be 52°. That given in the literature is 51°.[21] The product was thrown into the steam still with 100 c.c. of 15% HCl and steam was blown through until no more oil distilled over. The residue was poured out into a beaker and the dark red liquid layer immediately solidified. This was filtered off and broken up in a mortar. The filtrate yielded only a trace of precipitate when treated with alkali.

The red solid was found to be very slightly soluble in alcohol; but a sufficient quantity was used to dissolve it when hot. After two crystallizations the melting point was 135-37°. Subsequent

crystallizations apparently had no effect.

Analyses from several brominations gave the following:

Nitrogen found 3.07, 3.12, 3.02, 3.14, 2.8, 3.06%

Nitrogen calculated for $C_{13}H_8ONBr_3$ 3.22%

During the hydrolysis of the brominated Schiff base a quantity of white crystalline solid distilled over. This was collected and recrystallized. The melting point was found to be 104° and the product was found to dissolve readily in cold alkali. This product was evidently the monobrom salicylaldehyde which melts at 104°.[22] A mixed melting point confirmed this conclusion.

Some salicylaldehyde also distilled over.

Some of the brominated salicylidene aniline was then steam-distilled with dilute acid until the distillate was clear; and the residue was made alkaline with sodium hydroxide. The distillation was then continued for several hours, the distillate finally becoming clear.

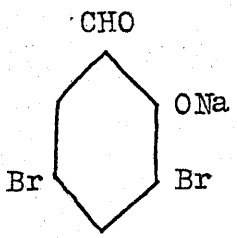
The solid which distilled over was filtered off and recrystallized from alcohol. The melting point was found to be 80°. That given in the literature

for 2:4 dibrom aniline is 79.5°. [23] Analysis for nitrogen gave the following results:

Nitrogen found 5.3%, 5.75%

Nitrogen calculated for $C_6H_5NBr_2$ 5.6%

The alkaline residue in the steam-distillation flask was filtered while hot and bright yellow crystals separated from the filtrate on cooling. The properties of this compound closely resemble those tiven by Brewster[24] for the sodium salt of 3:5 dibrom salicylaldehyde.



Some of this product was treated with dilute acid and the melting point of the product was found to be 83°. The melting point of 3:5 dibrom salicylaldehyde is 81-82°.[24]

As the red product obtained above seemed to be a tri brom salicylidene aniline another bromination was carried out using three moles of bromine instead of two. The product after hydrolysis melted at 173° and contained 2.7% nitrogen. It appears, therefore, that the result of bromination of salicylidene anilene is mixed products, some of the tetra brom

salicylidene aniline being formed when three moles of bromine are used.

In order to gain an idea of the possible products the following compounds were synthesized from the corresponding substituted aniline and salicylaldehydes:

(1) 3:5 dibrom salicylidene-para brom aniline; m.p.160°; color, red; given in literature, m.p. 160°.[24]

(2) 5 brom salicylidene-para brom aniline; m.p. 173°; color, yellow; not given in literature. Nitrogen found 4.00% nitrogen calc. 3.94%.

(3) 5 brom salicylidene-2:4 dibrom aniline; m.p. 152°;# color, yellow-brown; not given in literature.

Two other similar compounds are known: Salicylidene-para brom aniline, m.p. 112°.[21], and 2:5 dibrom salicylidene-aniline, m.p. 91°.[24] The latter product is reported to be insoluble in cold, dilute sodium hydroxide but slowly decomposed on boiling. These properties correspond with those of the red tribrom salicylidene aniline obtained from bromination of the unsubstituted Schiff base.

That the brominated salicylidene anilines are not readily hydrolyzed is not surprising since it has been found that substitution in the aldehyde

Only a very small quantity of this compound was obtained.

ring tends to stabilize the Schiff base. Thus, para nitro benzylidene bases are much more stable than simple benzylidene bases.[25]

However, as is shown below, not all salicylidene bases are stable toward hydrolyzing agents after bromination.

Salicylidene Beta Naphthyl Amine:-

Fourteen grams of beta naphthyl amine were mixed with twelve grams of salicylaldehyde and heated for two hours on the water bath. The liquid was then poured out into water and immediately solidified. This solid was washed with dilute alcohol and dilute acetic acid and dried. It was then brominated in carbon disulfide and hydrolyzed in alcohol. The product was immediately precipitated on cooling and was filtered off and washed with sodium carbonate solution. After washing with water and drying, it was boiled with alcohol. A small amount of orange-colored solid immediately precipitated out on cooling and was found to melt at 215-219°. On analysis this product gave the following results:

Nitrogen found 4.94%

Nitrogen calculated for $C_{13}H_{11}ONBr_2$ 3.92%

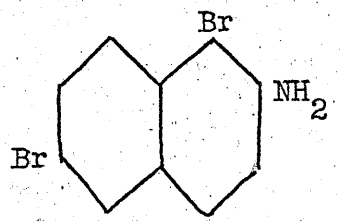
Nitrogen calculated for $C_{10}H_5NBr_2$ 4.65%

However, the greater part of the yield settled out only after dilution of the alcohol with water and standing for some time. This compound melted at 121-126° and gave the following results on analysis:

Nitrogen found 4.65% 4.02%

Nitrogen calculated for $C_{10}H_5N\ Br_2$ 4.65%

The product is, therefore, 1:6 dibrom beta naphthyl amine which melts at 122°.[7]



The brominated salicylidene beta naphthyl amine is evidently much less stable than the brominated salicylidene aniline.

CONCLUSIONS

These experiments bear out the theory that the bromine adds first to the nitrogen of the Schiff base, since an unstable addition product was found in each case. This product was found to be readily broken up by hot dilute acid and, in one case, by pyridine and alcohol (see meta chlor aniline). The brominated benzylidene naphthyl amines are strongly affected by water. The fact that the brominated salicylidene aniline was not readily hydrolyzed to an amine and an aldehyde has been attributed to the stabilizing effect of the hydroxyl group in the aldehyde. However, the nature of the addition product was readily changed by the addition of acid from an unstable, flocculent, brown precipitate to a red, crystalline solid. Some of the brominated bases cannot be hydrolyzed satisfactorily with dilute acid in water solution but yield good quantities of eadily workable products when hydrolyzed in alcohol to which a little acid has been added.

In no instance did a brominated benzaldehyde result from hydrolysis of a brominated benzylidene base. The salicylidene bases are evidently substituted

to some extent in the aldehyde ring. This does not indicate, however, that the bromine adds first to the double bond between carbon and nitrogen. It is very much more probable that the bromine in the aldehyde ring is substituted directly due to the influence of the phenolic group.

It has been shown that Wainscott's method of brominating the aromatic Schiff bases in general gives good results and fairly uniform products. The only exception encountered is benzylidene para xylidine which gives better results when brominated in chloroform.

A di-brominated amine is not the only brominated amine obtained but is the principal product except in the case of meta chlor aniline which gave an abundance of the tri brom meta chlor aniline and in the case of salicylidene aniline where the principal product evidently contains only two bromine atoms in the aldehyde ring. The mono and tri brom anilines are readily separated by boiling with dilute acid as described.

Finally, it has been shown that the position of the bromine in the amine ring after hydrolysis is the

same as that which it would occupy if the amine were brominated directly. This tends to strengthen the analogy between the Schiff bases and amines where bromine adds first to the amino nitrogen and then migrates to the ring.

BIBLIOGRAPHY

1. Schiff, A. 239, 384 (1887).
2. Frangen, J. Prak. Chem. 88, 755 (1913); 91, 295; 95, 160 (1917).
3. Hantzsch, B. 34, 836 (1901).
4. James and Judd, Soc. 105, 1427 (1914).
5. M. A. Berg, Bull. Soc. Chim. 37, 656-47 (1925).
6. L. Claisen, A. 237, 273 (1887).
7. T. A. Lawson, B. 18, 2424 (1885).
8. Claus and Philipson, J. Pr. Chem. 43, 48 (1891).
9. R. Mendola, B. 12, 1961 (1879).
10. R. Mendola, B. 11, 1906 (1878).
11. C. Philipp, B. 25, 3248 (1892).
12. C. Langer, A. 215, 112 (1882).
13. Wheeler and Valentine, Amer. Chem. Jour. 22, 271 (1899).
14. Hübner and Alsberg, A. 156, 312.
15. Chattaway and Orton B. 33, 2398.
16. Wurster and Nölting, B. 7, 1564 (1874).
17. Hübner, B. 10, 1709 (1877).
18. L. Pflug, A. 255, 169 (1889).
19. Nölting and Kohn, B. 19, 142 (1886).
20. Nölting and Kopp, B. 38, 3513 (1905).
21. Hantzsch and Schwab, B. 34, 832 (1901).
22. W. P. Bradley, B. 22, 1135 (1889).

23. P. Griefs, A. 121, 267 (1862).

24. C. M. Brewster, J. Am. Chem. Soc. 46, 2463 (1924).

25. Langman, Healy, and Dutt, Quant. J. Indian Chem. Soc. 4, 75 (1927).