80 cc. of benzene containing 0.5 cc. of water. Each solution was saturated with sulfurous dioxide and allowed to stand at ordinary temperatures in loosely corked flasks (since these experiments were tried before we had found that the quinhydrone crystals were deposited without any evaporation of the solvent). After four weeks the flask containing the iodoanil showed crystals, some of which were black like the quinhydrone, others brown like iodoanil, but, as the black crystals were no larger than the others, the darker color could not be due to greater thickness. This black color, which we have never observed with iodoanil alone, justifies us in inferring that the quinhydrone had been formed, and we were confirmed in this belief by the peculiarities in habit of the two sorts of crystals, for, while the black were usually terminated at both ends by two planes at an obtuse angle, the brown showed only one such termination, the other, if well developed, consisting of a single plane at right angles to the sides. From the solution of chloroanil there had been deposited large clumps of white prisms evidently tetrachlorohydroquinone mixed with a small amount of yellow unchanged chloroanil, while only a yellow deposit of bromoanil was obtained from the experiment with this compound. Neither with chloroanil nor the bromoanil was there any indication of a substance with a darker color than yellow.

Action of Iodoanil on Tetraiodohydroquinone.—To determine whether the formation of the quinhydrone required that the hydroquinone should be in the nascent state, a mixture of iodoanil and tetraiodohydroquinone, in the proportion of two molecules of the former to one of the latter, was dissolved in warm benzene. Upon cooling brown crystals of iodoanil separated and the liquid was then allowed to stand in a loosely corked flask for several weeks, when the crystals deposited were found to consist of long, slender, brown prisms and broader, black, prismatic plates, from which we infer that octoiodoquinhydrone had been formed in this case also, although in smaller quantity than in the experiment, in which the iodoanil was reduced by sulfurous acid.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

THE SPLITTING OF BENZHYDROLS BY THE ACTION OF BROMINE.[1]

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In the course of a research on certain substituted benzophenones and benzhydrols, the authors observed that when bromine was allowed to

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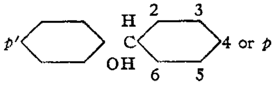
[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, Cambridge, Mass., U. S. A., for the degree of Doctor of Philosophy by Gustavus J. Esselen, Jr.

act on 4-aminobenzhydrol, in chloroform solution, a splitting took place, by which benzaldehyde was set free.[1] The amount of the last was small, and the principal reaction product was probably an anhydride of high molecular weight, such as that obtained by Kippenberg,[2] from 4-aminobenzhydrol by the action of hydrobromic acid. To a certain extent, however, the following reaction seemed to take place, although we were not able to isolate any bromoaniline,

$$C_6H_5.CH(OH).C_6H_4NH_2 + Br_2 = C_6H_5CHO + BrC_6H_4NH_2 + HBr.$$

As such a reaction is entirely new, we decided to investigate it further and so prepared 3,5-dibromo-4-aminobenzhydrol, which we considered would not undergo the Kippenberg anydride reaction. When this hydrol, in chloroform solution, was treated with two atoms of bromine, the products were found to be benzaldehyde, 2,4,6-tribromoaniline and hydrobromic acid, no other compounds being formed in amounts sufficient to be detected.

That the reaction is a general one is shown by the following table, giving the compounds which have been investigated, and the products they yielded when treated with bromine in chloroform solution. Hydrobromic acid was formed in every case together with the other products indicated.

Substituents in the benzhydrol.  	Products.
1. *p*-Amino	Benzaldehyde, *p*-bromoaniline(?) anhydride
2. 3,5-Dibromo-4-amino	Benzaldehyde, 2,4,6-tribromoaniline
3. 3-Methyl-4-amino	Benzaldehyde, 3,5-dibromo-2-toluidine
4. *p*'-Nitro-*p*-monomethylamino	*p*-Nitrobenzaldehyde, *o*,*p*-dibromomonomethylaniline
5. *p*-Dimethylamino	Benzaldehyde, *p*-bromodimethylaniline
6. 3-Bromo-4-dimethylamino	Benzaldehyde, *o*,*p*-dibromodimethylaniline
7. *p*'-Nitro-*p*-dimethylamino	*p*-Nitrobenzaldehyde, *p*-bromodimethylaniline
8. *p*,*p*'-Tetramethyldiamino	*p*-Dimethylaminobenzaldehyde, *p*-bromodimethylaniline
9. *p*'-Nitro-*p*-diethylamino	*p*-Nitrobenzaldehyde, *p*-bromodimethylaniline
10. 2-Amino-5-methyl	Benzaldehyde, 3,5-dibromo-4-toluidine
11. *m*-Amino	No splitting
12. Unsubstituted[3]	No splitting

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[1] THIS JOURNAL, **33**, 1135 (July, 1911).

[2] *Ber.*, **30**, 1135.

[3] Linnemann [*Ann.*, **133**, 11 (1865)] got no splitting with bromine sealed at 200°.

In Nos. 3, 4, and 10 in the above table, one molecular proportion of bromine split only half of the hydrol present, which is explained by the fact that in each case a dibromo compound was formed.

The usual solvent was dry chloroform, free from alcohol, but alcohol-free ether and absolute alcohol serve equally well. Ether has the advantage that the aldehyde product of the splitting remains in solution, while the hydrobromide of the amino part is precipitated, thus making the separation of the products, as a rule, easy.

In brief, it has been shown that benzhydrols, with an amino or alkylated amino group in the ortho or para position to the hydrol group, are split by the action of bromine into benzaldehyde or benzaldehyde derivatives, and a halogenated aniline derivative. Chlorine and iodine act similarly to bromine with such modifications, as the differences in nature of these three elements would lead one to expect, but neither gives so good results as bromine. Benzhydrol and *m*-aminobenzhydrol do not split under the influence of bromine. Finally the reaction does not depend on the solvent in which it is carried on.

This reaction has a very practical value for organic chemistry in determining the constitution of compounds belonging to certain classes, not only the benzhydrols or benzophenones containing an amino group in the ortho or para position, or benzhydrols in which such a group could be introduced, but also the derivatives of diphenylmethane, inasmuch as these, on oxidation with chromic acid, give the corresponding benzophenone compounds which, in turn, could be reduced to the benzhydrols with sodium or aluminum amalgam, and then split with bromine.

In looking through the literature for similar examples of splitting, only one was found in any way resembling the one under consideration. Weil[1] noticed that boiling with dilute mineral acid for several days breaks up *p,p'*-tetramethyldiaminobenzhydrol into dimethylaniline and *p*-dimethylaminobenzaldehyde, which latter condenses at once in the acid solution with unchanged hydrol or with dimethylaniline to form leuko-crystal violet, but when this splitting with acid is compared with the bromine splitting, several marked differences are apparent. The most striking is, that in the case of bromine the action takes place almost instantaneously even at 0°, whereas with the acid it takes several days at a temperature of about 100°. Another difference is that dimethylaniline is produced with the acid, where *p*-bromodimethylaniline is obtained in the bromine splitting. Finally some compounds, which are synthesized by heating *p*-nitrobenzaldehyde with an alkylated aniline at 100° in concentrated hydrochloric acid solution for forty hours, for example *p*-nitro-*p'*-dimethylaminobenzhydrol and *p*-nitro-*p'*-diethylaminobenzhydrol, break down at once when treated with bromine in chloroform. In these

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[1] *Ber.*, **27**, 3316 (1894).

cases there can be no doubt that the splitting is not due to acid or it would not be possible to synthesize the compounds in the manner in which they are prepared. Since the other examples of the splitting are analogous to these two, this evidence may be included with the rest to show that in no case is the splitting with which this work is concerned due to hydrobromic or other mineral acid, but is caused entirely by the action of the bromine.

The Mechanism of the Reaction.

Concerning the mechanism of the reaction whereby bromine splits ortho and para-aminobenzhydrols, Hantzsch and Graf[1] have shown that bromine, when allowed to act on an aromatic amine, first forms an unstable addition compound in which one molecule of bromine is directly added to nitrogen, and that this addition compound then rearranges to form the hydrobromide of a substitution product, from which the hydrobromic acid may or may not be split off according to the conditions.

If now our reaction proceeds in accordance with the work of Hantzsch and Graf, the primary product should be a compound of the general formula:

$$C_6H_5.CH(OH).C_6H_4NR_2Br.Br,$$

where R may be either hydrogen or an alkyl group. When the splitting was carried out at —80°, it was found possible to isolate intermediate compounds, which exhibited all the properties that would be expected from amine dibromides, some of which could be explained on no other basis except the assumption that they were amine dibromides. It may be objected that the splitting reaction might take place very quickly even at —80°, and that the supposed intermediate compounds were really perbromides of the bromoamine formed by the splitting. In answer to this, it is sufficient to consider the case of *p*-dimethylaminobenzhydrol and to point out that the perbromides of *p*-bromodimethylaniline are solids,[2] are comparatively stable at room temperature and form at 0°, whereas our compound in this case was an oil and did not form even at —20°. Accordingly it is clear that the substances in question must be considered as amine dibromides even though their instability at ordinary temperatures prevented an analysis to determine their exact composition.

The next question is obviously as to how the dibromide of an aminobenzhydrol can fit into a scheme which explains the splitting of aminobenzhydrols. It will be remembered that Hantzsch and Graf[3] were unable to isolate the dibromide of dimethylaniline, because of the great tendency for one atom of bromine to change places with the parahydrogen atom of the benzene ring, thereby forming the hydrobromide of *p*-bromo-

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[1] *Ann.*, **346**, 188 (1906).

[2] *Ibid.*, **346**, 195 (1906).

[3] *Loc. cit.*

dimethylaniline. This rearrangement was found to take place even at —40°. Since bromine exhibits so great a tendency to shift to the para position in the ring, it would not seem surprising if the second stage in the action of bromine on aminobenzhydrol consisted in an interchange of position between one of the added atoms of bromine and the group in the para position, *viz.*, $C_6H_5CH(OH)$. The compound thus formed would be represented by the formula: $BrC_6H_4N(R_2)(Br)—CH(OH)C_6H_5$.

Objection may be raised that the analogy is not complete; that the large group $C_6H_5CH(OH)$—could not be expected to shift with any such readiness as an atom of hydrogen, as in the case of dimethylaniline. The answer to this is, that, in order to be dislodged by the bromine, the group in the para position need only be united to the benzene nucleus by a force which is no stronger than that which binds an atom of hydrogen in a similar position. If such is the case, the work of Hantzsch and Graf already referred to shows that it will be replaced by the bromine. Chattaway[1] has further shown that the compound, $C_6H_5N(COC_6H_5)_2$, when heated, rearranges to a compound with the formula: $C_6H_5COC_6H_4NH—COC_6H_5$. In this case the group which rearranges is C_6H_5CO—, quite similar to the one with which we are dealing. If this rearranges in the molten solid, the rearrangement supposed for the bromine reaction in this paper ought to go much more readily when once started, since it is carried on in solution.

It may be well to consider if there is any further evidence, other than analogy, which indicates the occurrence of a rearrangement like that just outlined. The first thing that suggests itself is the fact that when the amine dibromides of the aminobenzhydrols were put on a watch glass or porous plate at ordinary temperatures, they were agitated by some internal disturbance which may well have been due to a readjustment or rearrangement of the forces within the molecule. A strong confirmation of the theory given above is that the splitting occurs with those benzhydrols where the amino or alkylated amino group is in the para or the ortho position, but does not occur when the amino group is in the meta position. Now, it is well known that halogen, rearranging from nitrogen, tends to go into the para position if possible, and if not, then to the ortho position, but never to the meta position.

Granting, then, that such a rearrangement takes place, it requires only that a molecule of hydrobromic acid be split off, to give the products actually obtained by experiment. This molecule of hydrobromic acid may, or may not, combine with the amine according to the conditions and the nature of the amine. The mechanism of the reaction would be then as follows:

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[1] *J. Chem. Soc.*, 85, 394 (1904).

$$C_6H_5CH(OH)C_6H_4NR_2 + 2Br \longrightarrow C_6H_5CH(OH).C_6H_4NR_2BrBr \longrightarrow$$
$$C_6H_4CH(OH).N(R_2)Br.C_6H_4Br \longrightarrow C_6H_5CHO + N(R_2)C_6H_4BrHBr.$$

Experimental Part.

The preparation, properties and action of bromine on *p*-aminobenzhydrol and 3,5-dibromo-4-aminobenzhydrol have been described in an earlier paper.[1]

3-Methyl-4-aminobenzhydrol.—The preparation of 3-methyl-4-aminobenzhydrol was effected by reducing 3-methyl-4-aminobenzophenone with sodium amalgam in alcoholic solution. The 3-methyl-4-aminobenzophenone was made according to the method of Chattaway[2] and Lewis by heating *o*-toluidine with benzoyl chloride in the presence of anhydrous zinc chloride and saponifying the resulting benzoyl derivative of 3-methyl-4-aminobenzophenone. In carrying out the reduction, one part of 3-methyl-4-aminobenzophenone was dissolved in twelve parts of alcohol and to the solution were added fifteen parts of three per cent. sodium amalgam. After standing at room temperature for several hours, the mixture was heated on a steam bath with a reflux condenser for six hours, five parts of water being added to the mixture after two and a half hours. At the end of six hours the solution was filtered hot and evaporated on a steam bath until crystallization began. It was then cooled and the crystals which formed were filtered off and dried. They were crystallized from a mixture of one part of alcohol with three parts of water and a drop or two of twice normal sodium hydroxide solution. Hot benzene, hot naphtha or hot carbon tetrachloride can also be used, but none of these work so well as the dilute alcohol just referred to.

Properties.—3-Methyl-4-aminobenzhydrol crystallizes in white needles which melt at 110°. It is soluble in methyl and ethyl alcohols, ether, hot benzene, hot naphtha, chloroform, acetone, and hot carbon tetrachloride. It is insoluble in water. Concentrated nitric acid dissolves it, forming a solution which is yellow at ordinary temperature but turns red on boiling. Concentrated hydrochloric acid converts it into an amorphous body which is not soluble even in boiling sulfuric acid. It dissolves slowly in cold, concentrated sulfuric acid to form a deep red solution which darkens on heating. Cold, glacial acetic acid forms a solution with a pale red tint. On boiling, this color changes to green and on subsequent cooling a greenish yellow solid is produced which does not melt, but chars at about 210°. These facts seem to point to the formation of an anhydride, analogous to the one formed in the case of *p*-aminobenzhydrol under similar conditions. A further indication of this is the fact that, if 3-methyl-4-aminobenzhydrol is dissolved in hot water and the resulting solution boiled so that the acid fumes of the laboratory have access

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[1] THIS JOURNAL, **33**, 1138 (1911).

[2] *J. Chem. Soc.*, **85**, 591 (1904).

to it, a white, amorphous precipitate begins to form after a few minutes. This is the reason why the liquid from which the body is crystallized is always kept slightly alkaline.

Calculated for $C_{14}H_{15}ON$: N, 6.57%; found, 6.59%.

Action of Bromine on 3-Methyl-4-aminobenzhydrol.—3.5 g. of 3-methyl-4-aminobenzhydrol were dissolved in 70 cc. of chloroform (which had been washed three times with water and thoroughly dried) and treated with 2.63 g. (corresponding to two molecules) of bromine. The action generated a considerable amount of heat. After standing a minute or two, a white precipitate appeared in the solution and was filtered off, but it was so very small in amount that it could not be identified. The chloroform filtrate was evaporated in a rapid current of air, leaving an oily residue with a benzaldehyde odor, which was shaken with 1 : 4-hydrochloric acid. The resulting solution was almost neutralized with sodium hydroxide, extracted with ether and evaporated, leaving an oil, which was proved to be benzaldehyde by converting it to the phenylhydrazone. This, after four crystallizations, formed white, shining needles, which turned pink when exposed to the light, and melted at 153–154°, thus corresponding to the phenylhydrazone of benzaldehyde.

The residue from the extraction with hydrochloric acid was covered with very dilute acid and distilled with steam. A pale, yellow oil came over which solidified to a pale green, crystalline solid. It melted at 46.5° and sublimed to form white needles which contained halogen and melted at 46.5–47°. After two crystallizations from 25% alcohol and one from 35% alcohol, it melted at exactly the same temperature. It appeared that we were dealing with 3,5-dibromo-2-toluidine, which melts at 45–46°, according to Neville and Winther,[1] and at 50° according to Wroblevsky,[2] the latter figure being given also by Möhlau and Oehmichen.[3] After the elaborate purification process which it had undergone there was not enough of this dibromotoluidine left to analyze. Accordingly some 3,5-dibromo-2-toluidine was synthesized by treating *o*-toluidine dissolved in chloroform with bromine. The conditions of the synthesis were thus almost identical with those under which the compound was formed, when 3-methyl-4-aminobenzhydrol was split by the action of bromine. One sample of the resulting hydrobromide of 3,5-dibromo-2-toluidine was converted to the free base and purified by crystallizing from hot 50% alcohol. It then had the constant melting point 47°.

Calc. for $C_7H_7NBr_2$: Br, 60.35; found, 60.69.

Action of Bromine on p-Nitro-p′-methylaminobenzhydrol.—The method used in preparing *p*-nitro-*p*′-methylaminobenzhydrol was that of Al-

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[1] *Ber.*, 13, 966 (1880).

[2] *Ann.*, 168, 187 (1873).

[3] *J. prakt. Chem.*, [2] 24, 478 (1881).

brecht,[1] which consists essentially in heating *p*-nitrobenzaldehyde with monomethyl aniline in the presence of an excess of concentrated hydrochloric acid for forty hours on a steam bath. On dilution with water the unchanged nitrobenzaldehyde separated out and was filtered off. The filtrate was made alkaline with sodium hydroxide solution, the resulting precipitate distilled with steam to free it from unchanged methylaniline, and the residue was crystallized from 25% alcohol, giving fine, yellow needles, which melted at 113°, as against 108°, given by Albrecht as the melting point of the same compound.

In studying the action of bromine on *p*-nitro-*p'*-methylaminobenzhydrol, 2.5 g. of the substance were dissolved in 60 cc. of chloroform and to the solution 1.5 g. (corresponding to one molecule) of bromine were added. A small amount of a black oil was thrown out of solution at once. It was not volatile with steam and its identity could not be established. The solution was poured off from the black oil and the chloroform evaporated, leaving a green, partly crystalline substance. This was washed three times with ether and the insoluble residue distilled with steam, yielding a very small amount of yellow oil and a yellow solution. The oil was removed and combined with more of the same obtained from the ether washings, as will be described in a moment. On cooling the yellow solution, crystals separated out, which, after four crystallizations from water, formed long, slender, white needles and melted at 105°. They were thus identified as *p*-nitrobenzaldehyde, the melting point of which is given by Otto Fischer as 106°.[2] Our compound also had the characteristic aldehyde odor which he mentions. The ether extract of the residue left from the evaporation of the chloroform was evaporated and the resulting oil distilled with steam. The yellow oil which came over solidified on cooling, and when boiled with water, a small part of it dissolved, the solution depositing, when cool, a very small amount of pale yellow needles which proved to be *p*-nitrobenzaldehyde. The part insoluble in water was crystallized from dilute alcohol, forming white shining plates with a yellowish tinge. They were recognized as *o*-*p*-dibromomonomethyl aniline, melted at 47°, and had the other properties of that compound as given by Fries.[3]

Action of Bromine on p-Dimethylaminobenzhydrol.—The *p*-dimethylaminobenzhydrol used in this work was made by reducing *p*-dimethylaminobenzophenone with sodium amalgam according to the directions of Albrecht.[4] The most convenient method for preparing *p*-dimethylaminobenzophenone consisted in heating benzanilide with dimethylaniline in the presence of phosphorus oxychloride and pouring the product

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[1] *Ber.*, 21, 3292 (1888).

[2] *Ibid.*, 14, 2525 (1881).

[3] *Ibid.*, 37, 2346 (1904).

[4] *Ibid.*, 21, 3293 (1888).

into water;[1] although the first *p*-dimethylaminobenzophenone used in this work was made according to the method of Döbner,[2] *viz.*, heating *p*-aminobenzophenone in a sealed tube with methyl alcohol and methyl iodide.

Five grams of *p*-dimethylaminobenzhydrol were dissolved in 80 cc. of chloroform and two molecular proportions of bromine added. Dry hydrogen chloride was then passed into the solution in excess to form the hydrochloride of any amine present. When the chloroform was evaporated, a green liquid was left, from which a pale yellow oil was extracted by ether. This yellow oil had the characteristic odor of benzaldehyde and boiled at 179°, which is the value given by Kopp as the boiling point of benzaldehyde.[3] In another experiment the benzaldehyde was identified by forming the characteristic phenylhydrazone which melted at 156°. The part of the green liquid insoluble in ether was dissolved in absolute alcohol and made alkaline by the addition of 4.5 g. of sodium hydroxide. The residue left after the evaporation of the alcohol was distilled with steam, giving white, waxy plates. Since these smelled noticeably of benzaldehyde, they were spread out in a thin layer and exposed to the air for three days, during which time the benzaldehyde was oxidized to benzoic acid. To get rid of this acid, the solid was washed, first with 6% sodium hydroxide solution and then with pure water. After being subjected to steam distillation, the substance melted at 53° and was analyzed for bromine.

Calc. for $C_8H_{10}NBr$: Br, 39.99; found, 40.37.

Thus the compound was parabromodimethylaniline.

Action of Bromine on p-Dimethylaminobenzhydrol at –80°.—In studying the action of bromine on *p*-dimethylaminobenzhydrol at low temperatures two kinds of experiments were performed. In the first an amount of bromine proportional to two atoms was used and in the second an amount proportional to one atom. For example, in an experiment of the first kind 2 g. of *p*-dimethylaminobenzhydrol were dissolved in 5 cc. of chloroform in a small Erlenmeyer flask, and cooled in a mixture of ether and carbon dioxide snow. A solution of 1.42 g. of bromine in 5 cc. of chloroform was prepared and similarly cooled. When this was added to the other solution a dark red oil separated out as soon as the one solution came in contact with the other. A little of the red oil taken out on a platinum spatula and put on a porous plate at room temperature turned to a very pale red color and was apparently agitated by some reaction for a few seconds. After this the odor of benzaldehyde was noticeable. In some cases a few bubbles of gas appeared during the agitation on the porous

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[1] German patent, No. 41,751; Friedländer, I, 44.

[2] *Ann.*, **210**, 270 (1881).

[3] *Ibid.*, **94**, 314 (1855).

plate, probably due to the vaporization by the heat of reaction, of the small film of chloroform which still clung to the oil. The chloroform was now poured off from the main part of the oil in the original flask and acetone added in its place. The oil dissolved slowly, and at the end of an hour or so, the odor of benzaldehyde was unmistakable, as was also the characteristic effect on the eyes and nose of bromoacetone.

In an experiment of the second class, solutions of 2 g. of *p*-dimethylaminobenzhydrol and 0.71 g. of bromine, each in 5 cc. of chloroform, were prepared, cooled and mixed as before. A little of the red oil which formed immediately was taken out on a platinum spatula and quickly put into an aqueous solution of starch and potassium iodide, cooled to its freezing point. The characteristic blue color produced by free iodine was developed at once and was further identified by the fact that arsenious acid caused it to disappear. In order to make absolutley sure that the test was due to an amine dibromide and not to unused bromine, some of the red oil was prepared at –80°, exactly as it was in the first experiment described above. The mother liquor was then poured off and the oil was washed three times with chloroform which had been shaken out with water, carefully dried, and cooled to its freezing point. The third washing was shaken with an aqueous solution of starch and potassic iodide, but only an exceedingly faint bluish tinge was developed, showing that all the free bromine, if any had not reacted, had been removed. A little of the red oil was then put into a similar starch-potassic iodide solution and a very deep blue color was developed which clearly showed that the oil was an amine dibromide.

3-Bromo-4-dimethylaminobenzophenone.—The simplest procedure for preparing 3-bromo-4-dimethylaminobenzophenone was found to be the following: 12 g. of *p*-dimethylaminobenzophenone were dissolved in 82 cc. of ordinary chloroform and to the solution was added 8.5 g. (corresponding to one molecule) of bromine, the color of the bromine disappearing as soon as it dissolved in the chloroform. After standing for a short time the chloroform was evaporated on a steam bath, leaving a colorless oil which was crystallized from 80% alcohol. Yield, 10 grams.

3-Bromo-4-dimethylaminobenzophenone was first obtained in an experiment, the object of which was to prepare 3-5-dibromo-4-dimethyl aminobenzophenone. It was found that but one atom of bromine could be introduced into 4-dimethylaminobenzophenone, an excess of bromine giving only a perbromide from which acetone, alcohol and potash form the above monobromo derivative. Nor did we succeed in producing the 3-5-dibromo-4-dimethylaminobenzophenone by methylation of 3-5-dibromo-4-aminobenzophenone.

Properties.—3-Bromo-4-dimethylaminobenzophenone can easily be crystallized from hot alcohol or hot naphtha. It forms colorless, transparent rhombic plates when allowed to crystallize by the spontaneous evaporation of a solvent. When crystallized from hot alcohol, it forms white, shining crystals, and melts when pure at 80°. It is soluble in ether, benzene, chloroform, carbon tetrachloride, glacial acetic acid, acetone, hot alcohol, and hot naphtha, but insoluble in water.

3-Bromo-4-dimethylaminobenzhydrol.—The first reducing agent tried in the reduction of 3-bromo-4-dimethylaminobenzophenone to the corresponding hydrol was zinc and acetic acid. This, however, did not apparently accomplish the desired result. Aluminum amalgam was next tried in the following manner. A solution of five grams of 3-bromo-4-dimethylaminobenzophenone in 150 cc. of alcohol was prepared and treated with aluminum amalgam from 25 grams of aluminum punchings. The mixture stood at room temperature for four hours and there was then added to it 8 cc. of water and aluminum amalgam from 13 g. of aluminum punchings. After standing for about eighteen hours longer, the solution was filtered from aluminum hydroxide, aluminum, and mercury, and the precipitate was washed with warm alcohol. (If the mixture was heated to the temperature of the steam bath for any length of time during the reduction, a dark green color was developed which did not appear if the reduction was carried out at the ordinary temperature of the room. In one such instance where the green color was developed quite strongly, a faint odor of benzaldehyde seemed to be perceptible after the evaporation of the alcohol.) The alcoholic filtrate was evaporated on a steam bath, leaving a yellow oil which contained halogen and gave benzaldehyde when treated with bromine in chloroform. All attempts to crystallize it, however, were in vain. A sample was prepared and dissolved in ether. The ethereal solution was dried, by standing over fused calcium chloride several days, and was then filtered and the ether evaporated carefully on a steam bath. After the residual oil had been dried *in vacuo* over stick potassium hydroxide for forty-eight hours, it was analyzed with the following results:

Calc. for $C_{15}H_{16}ONBr$: Br, 26.12%; found, 24.88%.

Properties.—3-Bromo-4-dimethylaminobenzhydrol is a straw colored, viscous oil which is not volatile with steam, and boils with decomposition at about 275° under a pressure of 55–60° mm. A certain amount of charring accompanies the distillation. It is miscible with ether, benzene, hot naphtha, hot alcohol, chloroform, carbon tetrachloride, acetone, and glacial acetic acid, but not miscible with water.

Action of Bromine on 3-Bromo-4-dimethylaminobenzhydrol.—2 g. of 3-bromo-4-dimethylaminobenzhydrol were dissolved in 10 cc. of washed dried chloroform and to the solution was added an amount of bromine corresponding to two atoms. A red oil was thrown out of solution at once, but dissolved when stirred up for a few seconds. After the chloroform had been evaporated in a rapid stream of air, a dark brown oil was left, from which ether extracted a yellow oil which had the odor of benzaldehyde and which gave a phenylhydrazone melting at 150° after one crystallization. The oil which did not dissolve in the ether was covered with water, rendered slightly acid with sulfuric acid, and distilled with steam. The colorless oil which came over with the water was identified as benzaldehyde by forming its phenylhydrazone. When there was no longer any suspended material in the distilling flask, the receivers were changed, the acid liquid in the boiling flask was made barely alkaline and the steam distillation continued. A white oil now came over which had the odor of *o*-*p*-dibromodimethylaniline. There can be no doubt but that the compound was really *o*-*p*-dibromodimethylaniline, but through an accident the material was lost, and further study was not possible.

Action of Bromine on 3-Bromo-4-dimethylaminobenzhydrol at –80°.—The action of bromine on 3-bromo-4-dimethylaminobenzhydrol at –80° was tried in exactly the same way as the last experiment described under the heading "Action of Bromine on *p*-Dimethylaminobenzhydrol at –80°." The only difference was that in this case a red solid was produced when the bromine was added where formerly a red oil was formed. The solid behaved exactly as did the oil, showing those properties which could be expected if the bromine had added to the nitrogen, but it was so unstable at ordinary temperatures that an analysis was quite out of the question.

Action of Bromine on p-Nitro-p′-dimethylaminobenzhydrol.—Four grams of *p*-nitro-*p*′-dimethylaminobenzhydrol were dissolved in 30 cc. of chloroform and 2.35 g. (corresponding to one molecule) of bromine were added and allowed to stand for a little more than an hour. The crystalline residue left after evaporating the chloroform was washed with ether several times, and the ether distilled, leaving a yellow solid with an aromatic odor which, when crystallized from water six times, formed long, pale yellow needles, melting at 105°, and corresponding entirely with the *p*-nitrobenzaldehyde described by Otto Fischer.[1] The part of the reaction product insoluble in ether was dissolved in an alcoholic solution of sodium hydroxide, the alcohol was evaporated, the residue extracted with ether, and dry hydrogen chloride was then passed into the ethereal extract. The oil which formed was separated from the solution, covered with dilute alkali, and distilled with steam. The white solid which crystallized from the distillate in waxy plates contained halogen and was purified by three crystallizations from alcohol, when it had the melting point 54°. This combined with its unmistakable odor and its other properties, identified it as *p*-bromodimethylaniline. A portion of the reaction mixture which was evaporated at once also showed the presence of *p*-bromodimethylaniline, showing that our splitting took place very quickly.

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[1] *Ber.*, **14**, 2525 (1881).

The *p*-nitro-*p*′-dimethylaminobenzhydrol used in the work which has just been described was prepared by condensing dimethylaniline with *p*-nitrobenzaldehyde in the presence of an excess of hydrochloric acid.[1] The product was purified by crystallizing it from alcohol after the excess of dimethylaniline had been driven off by a rapid current of steam.

Action of Bromine on p-p′-Tetramethyldiaminobenzhydrol.—In studying the action of bromine on *p*-*p*′-tetramethyldiaminobenzhydrol, it was found that the temperature played quite an important part in determining how far the reaction went. If the chloroform, after the addition of the bromine to the chloroform solution of the benzhydrol, was evaporated on the steam bath, *p*-dimethylaminobenzaldehyde was identified without difficulty as one of the products of the reaction, but the other was a blue solid which behaved like a dye analogous to crystal violet, and no *p*-bromodimethylaniline could be found, although many varied attempts were made to detect it. However, this result was obtained as follows: 7.5 g. of *p*-*p*′-tetramethyldiaminobenzhydrol (prepared by reducing Michler's ketone with sodium amalgam[2]) were dissolved in 50 cc. of chloroform and treated with 4.4 g. of bromine, which was proportional to one molecule. Heat was generated by the reaction and the solution turned dark blue in color. On evaporating the chloroform in a rapid current of air, at room temperature instead of on the steam bath, a blue crystalline mass was left which had an odor like *p*-bromodimethylaniline. It was distilled with steam and the distillate collected in three fractions of about 300 cc. each. In the first fraction, on cooling, white waxy plates formed, which, after three crystallizations from alcohol, melted at 54° and had the characteristic odor of *p*-bromodimethylaniline.

Calc. for $C_8H_{10}NBr$; Br, 39.99; found, 40.33%.

The second fraction of the distillate, after a small amount of *p*-bromodimethylaniline had been filtered out, was treated with a few drops of alcohol and then with a little phenylhydrazine, which produced a white precipitate. When crystallized four times from water, this precipitate formed pale yellow, shining needles, which melted at 146.5° and corresponded in their properties with the phenylhydrazone of *p*-dimethylaminobenzaldehyde, which melts according to Knöfler and Boessneck[3] at 148°. The presence of *p*-dimethylaminobenzaldehyde in the third fraction of the distillate was shown by adding, after slight acidification with hydrochloric acid, a few drops of benzidine in water which produced a yellow color and at the end of about three-quarters of an hour the brick-red precipitate characteristic of *p*-dimethylaminobenzaldehyde according to Weil.[4]

[1] Albrecht, *Ber.*, **21**, 3292 (1888); German patent, No. 45,806.

[2] Nathanson and Müller, *Ber.*, **22**, 1879 1889).

[3] *Ber*, **20**, 3195 (1887).

[4] *Ibid.*, **27**, 3317 (1894).

Action of Bromine on p-Nitro-p'-diethylaminobenzhydrol.—In preparing the *p*-nitro-*p'*-diethylaminobenzhydrol which was used in this work, the method of Albrecht[1] was used, consisting in condensing *p*-nitrobenzaldehyde with diethylaniline in the presence of an excess of hydrochloric acid. 1.4 g. of *p*-nitro-*p'*-diethylaminobenzhydrol were dissolved in 10 cc. of dry chloroform and an amount of bromine corresponding to one molecule was added. The chloroform was evaporated in a rapid current of air, leaving a yellowish crystalline residue. Ether extracted from this a solid, which, after five crystallizations from water, melted at 105° and was identical in its other properties with the *p*-nitrobenzaldehyde described by O. Fischer. The residue, left after washing with ether, was subjected to steam distillation, first from a dilute sulfuric acid solution to get rid of the remaining *p*-nitrobenzaldehyde, and later from a slightly alkaline solution, yielding a sweet-smelling, colorless oil, which crystallized on cooling to form cream-colored plates containing halogen. When crystallized once from alcohol it formed white needles which melted at 33° and corresponded in every way with the *p*-bromodiethylanilin described by Claus and Howitz.[2]

2-Amino-5-methylbenzhydrol.—3-Methyl-4-aminobenzophenone was made by heating *p*-toluidine with benzoyl chloride, in the presence of anhydrous zinc chloride, for a number of hours.[3] After a saponification with alcoholic hydrochloric acid and removal of ethyl benzoate and tarry matters, the 3-methyl-4-aminobenzophenone was obtained by means of a long-continued steam distillation. In reducing this to the benzhydrol one part was dissolved in twelve parts of alcohol and fifteen parts of 3% sodium amalgam were added. After standing for two or three hours at room temperature, the mixture was boiled under a return condenser for six hours or until all the amalgam was exhausted, four parts of water being added at the end of three hours of heating. The solution was filtered hot and evaporated on a steam bath to about half of its original volume, when an oil separated out, and, on cooling, this solidified in white, radiating, circular clumps, which were crystallized from a mixture of one part of alcohol to four of water, the mixture being made alkaline with a few drops of twice normal sodium hydroxide. Two or three crystallizations were sufficient for purification. This compound was 2-amino-5-methylbenzhydrol.

Calc. for $C_{14}H_{15}NO$: N 6.57; found 6.62, 6.65%.

Properties.—When crystallized from slightly alkaline 20% alcohol, 2-amino-5-methylbenzhydrol forms white, feathery crystals or small, shining transparent rhombohedra. When dissolved in alcohol and al-

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[1] *Loc. cit.*

[2] *Ber.*, 17, 1327 (1884).

[3] Chattaway and Lewis, *J. Chem. Soc.*, 85, 594 (1904).

lowed to crystallize undisturbed by the spontaneous evaporation of the solvent, it forms large, well-formed transparent rhombohedra. It melts, when pure, at 107°. It is soluble in alcohol, ether, benzene, chloroform, acetone, glacial acetic acid, hot naphtha, carbon tetrachloride (somewhat soluble in the cold also) and hot water. It is only very slightly soluble in cold water or cold naphtha. Concentrated nitric acid dissolves 2-amino-5-methylbenzhydrol in the cold, forming a pale yellow solution which turns a deeper shade on boiling. When treated with cold concentrated hydrochloric acid it seems to dissolve, but in a few seconds a turbidity appears which dissolves on boiling, but reappears when the solution is cooled. Concentrated sulfuric acid dissolves it to form a red solution, which chars when heated.

Action of Bromine on 2-Amino-5-methylbenzhydrol.—In this experiment, the object of which was to see if an amino group in the ortho position to the hydrol group behaved like one in the para position, 2.1 g. of 2-amino-5-methylbenzhydrol were dissolved in 20 cc. of chloroform. On the addition of 1.58 g. (one molecule) of bromine a noticeable amount of heat was generated. The chloroform was evaporated at once by a stream of air, leaving a yellow oil which had the odor of benzaldehyde. It was washed five times with 20 cc. portions of 1 : 1 hydrochloric acid, leaving an insoluble residue which was not volatile with steam, being probably, for the most part, unchanged 2-amino-5-methylbenzhydrol. The hydrochloric acid washings were subjected to a steam distillation, and white needles were obtained, melting at 73°, and identical in every respect with the 3,5-dibromo-4-toluidine of Wroblewsky.[1] Nothing was obtained by further distilling after addition of an alkali. The filtrate from the white needles was proven to contain benzaldehyde by the formation of its phenylhydrazone[2] melting at 155.5°.

Meta-aminobenzhydrol.—*m*-Aminobenzophenone was made as follows: The chloride of *m*-nitrobenzoic[3] acid was condensed with pure benzene by means of anhydrous aluminum chloride.[4] It was found that only about one-third the amount of aluminum chloride given in the literature was needed. The resulting *m*-nitrobenzophenone was then converted to *m*-aminobenzophenone by reduction with stannous chloride in alcoholic hydrochloric acid. To reduce *m*-aminobenzophenone to *m*-aminobenzhydrol, one part of the former was dissolved in thirty-five parts of alcohol and twelve parts of 3% sodium amalgam were added. After standing over night at the ordinary temperature of the room, the mixture was heated with reflux condenser for two and a half hours and the procedure

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[1] *Ann.*, **168**, 188 (1873).

[2] *Loc. cit.*

[3] *Ber.*, **12**, 1943 (1870).

[4] *Ibid.*, **18**, 2401 (1886).

repeated. The solution was then filtered hot and evaporated to a syrupy consistency. When diluted with water and allowed to stand in a cool place, a white solid formed, which was purified by repeated crystallization from water or from a mixture of one part of alcohol to nine parts of water.

Calc. for $C_{13}H_{13}ON$: N, 7.04; found, 6.98%.

Properties.—Meta-aminobenzhydrol is a white solid which crystallizes in radiating clusters of needles or in small, transparent rhombohedra. It is soluble in alcohol, ether, benzene, chloroform, acetone, and glacial acetic acid, but practically insoluble in cold water, cold naphtha, and cold carbon tetrachloride. It is, however, soluble in the last three solvents hot. The melting point of *m*-aminobenzhydrol is a little peculiar. The substance usually melts when pure at 78°. In some cases, after a melting point of 78° had been obtained, another crystallization gave a solid which softened a little at 64°, but did not melt until a temperature of 76–77° was reached. All the crystallizations were carried out apparently under the same conditions, and the slight variation, if any, which caused the production of solids with different melting points could not be detected. It seems possible that the variation may be due to water of crystallization. In support of this idea it may be noted that a sample of the solid which melted at 64° was allowed to stand in a desiccator over caustic potash for ten days, after which it melted at 77°.

Action of Bromine on m-Aminobenzhydrol.—Bromine in chloroform solution when added to chloroform solutions of *m*-aminobenzhydrol, yielded nothing other than a yellow oil, which refused to crystallize. Experiments were carried out, in both hot and cold solvents, also using an excess of bromine, but with no better result. The reaction product certainly contained no benzaldehyde. It might well have been an anhydride formed by elimination of water from the hydroxyl and amino groups, analogous to the anhydride of Kippenberg, but this was not proved. However, the important point was established that *m*-aminobenzhydrol does not split down into benzaldehyde and bromoaniline under the influence of bromine.

Action of Bromine on Benzhydrol.—No splitting of benzhydrol was brought about by bromine, although tried under various conditions. Linneman[1] states that benzhydrol, when heated with bromine in a sealed tube for several hours at 200°, yields dibromobenzhydrol.

Action of Chlorine on p-Dimethylaminobenzhydrol.—A stream of dry chlorine gas, at the rate of 150 bubbles per minute, was passed for four minutes through a solution of 2.5 g. of *p*-dimethylaminobenzhydrol in 15 cc. of chloroform. The chlorine was generated by the action of hydrochloric acid on bleaching powder. It was freed from hydrochloric acid

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[1] *Ann.*, 133, 11 (1865).

by passing through a tower containing water and then dried by concentrated sulphuric acid. A considerable amount of heat was generated and the solution took on a slight green tinge. At the end of the four minutes the chloroform was evaporated in a rapid stream of air, the last traces being driven off at 100°. A green oil remained which had the odor of benzaldehyde. The odor was not very strong, but still unmistakable. The oil was washed three times with boiling ether, which removed a very small amount of a yellow oil with the benzaldehyde odor. The residue, insoluble in ether, when subjected to a steam distillation, from either very dilute acid or very dilute alkali, gave a small amount of a colorless oil which had an odor not unlike *p*-bromodimethylaniline and probably was *p*-chlorodimethylaniline. A non-volatile residue was left which was apparently, for the most part, *p*-dimethylaminobenzhydrol, since it gave the characteristic splitting with bromine in chloroform solution. From this experiment, it seemed probable that a splitting had occurred, inasmuch as the odor of benzaldehyde was noticeable at so many points in the procedure, but that the chlorine had acted further to form other products which could not be readily identified. Several modifications of the above procedure were tried, and in one case the temperature of the hydrol solution was maintained at -70-80°, but no better success attended these efforts.

Action of Iodine on p-Dimethylaminobenzhydrol.—Iodine in chloroform solution split *p*-dimethylaminobenzhydrol into benzaldehyde and other substances which could not be identified. The reaction does not proceed at all smoothly, and although tried under widely varying conditions only benzaldehyde was isolated. The latter was recognized through its odor, and the physical properties of its phenylhydrazone.

Use of Solvents Other than Chloroform.—*p*-Dimethylaminobenzhydrol in absolute ether solution, when treated with bromine in absolute ether, was at once split into benzaldehyde and the hydrobromide of parabromodimethylaniline, the former remaining in solution, the latter being thrown down as a reddish precipitate. The benzaldehyde was identified by conversion into its phenylhydrazone. The hydrobromide of parabromodimethylaniline was decomposed by alkali, giving the free base which was identified by its physical properties. The splitting took place equally well when absolute alcohol was employed as the solvent. In this case, after distilling off the alcohol, the two products were separated, first by distilling from acid aqueous solution which gave benzaldehyde, and second from alkaline solution, which gave the parabromodimethylaniline.

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