The Action of Benzoacetic Anhydride upon Acetonedicarboxylic Acid.—This anhydride was prepared to the method of Gerhardt[1] but is difficult to obtain in a high degree of purity. When acetonedicarboxylic acid is dissolved in this anhydride, warmed upon a steam bath, immediate action ensues. After a few minutes the red colored product was mixed with ether in excess and the undissolved portion filtered off. This precipitate, however, can not be dried, owing to its great tendency for decomposition. It may be preserved under ether for a short time. Several attempts were made to bring about a condensation in its molecule—supposedly a benzoylacetylacetonedicarboxylic acid—to form a benzoyl methylpyronone derivative of similar structure to dehydroacetic acid. No positive results, however, were obtained, and owing to the difficulty in securing what may be called the pure benzoacetic anhydride, no further work was attempted in this direction.

ANN ARBOR, MICHIGAN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

THE FORMATION OF BENZALDEHYDE AND 2,4,6-TRIBROMOANILINE FROM 3,5-DIBROMO-4-AMINOBENZHYDROL BY THE ACTION OF BROMINE.

BY LATHAM CLARKE AND GUSTAVUS J. ESSELEN, JR.

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While engaged on the study of certain bromine derivatives of 4-aminobenzophenone and 4-aminobenzhydrol, the following experiment was performed.

Five grams of 4-aminobenzhydrol (prepared by reducing 4-aminobenzophenone with sodium amalgam in alcoholic solution)[2] were dissolved in 150 cc. of washed and dried chloroform and to the solution 4 grams (two atoms) of bromine were added. A precipitate was thrown down and soon clotted together to form what appeared under a magnifying glass as a mixture of yellowish crystals and a yellow tarry mass. This precipitate was filtered off but could not be made to yield a crystalline substance—water, ether, acetone, naphtha, benzene, ethyl alcohol, chloroform, glacial acetic acid and ethylene dibromide were tried in vain. The material was soluble in alcohol and when the latter was evaporated off, a dark yellow jelly remained which had the odor of benzaldehyde. No pure products could be obtained but this was probably due to the presence of an anhydride of high molecular weight, identical with or analogous to that described by Kippenberg,[3] and formed from 4-aminobenzhydrol by the action of hydrobromic acid. In our case hydro-

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[1] *Ann.*, 87, 81 (1853).

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

[3] *Ibid.*, 30, 1137, 1138.

bromic acid was produced and liberated in small amounts on adding the bromine to the solution of the 4-aminobenzhydrol.

Subsequent experiments always gave a noticeable odor of benzaldehyde when the solvent was evaporated, but on account of the unmanageable nature of the reaction product benzaldehyde could not be isolated.

It seemed, however, as if a side reaction had taken place whereby the benzaldehyde had been formed by a splitting of the 4-aminobenzhydrol in the following manner,

$$C_6H_4—CH(O\vdots H)—C_6H_4NH_2 + Br_2 = C_6H_5—CHO + HBr + BrC_6H_4NH_2,$$

giving benzaldehyde, para bromaniline and hydrobromic acid. We had evidence of benzaldehyde and hydrobromic acid, but could detect no *p*-bromoaniline.

In order to ascertain whether such a reaction would take place in other cases or not, we decided to prepare 2,5-dibromo-4-aminobenzhydrol and to treat this with bromine. In this case the presence of the two atoms of bromine would probably prevent the formation of a compound analogous to Kippenberg's anhydride, and unhampered by this reaction we should be able to study the action of the bromine on the hydrol grouping, if such took place.

We therefore synthesized 2,5-dibromo-4-aminobenzhydrol by preparing first, 4-aminobenzophenone; treating this with four atoms of bromine gave 2,5-dibromo-4-aminobenzophenone,[1] and this when reduced with aluminum amalgam yielded the desired 2,5-dibromo-4-aminobenzhydrol. Summarizing these reactions:

$C_6H_5.CO.C_6H_4NH_2$, *p*-aminobenzophenone
$C_6H_5.CO.C_6H_2Br_2NH_2$, 3,5-dibromo-4-aminobenzophene
$C_6H_5CH(OH)C_6H_2Br_2NH_2$, 3,5-dibromo-4-aminobenzhydrol.

3,5-Dibromo-4-aminobenzhydrol was then treated in chloroform solution with two atoms of bromine, and thereby were produced, benzaldehyde, 2,4,6-tribromoaniline and hydrobromic acid. No other compounds were formed sufficient in amount to be detected. The benzaldehyde was identified in addition to its ordinary properties by conversion into the phenylhydrazone. From the original reaction mixture by passing into the solution dry gaseous hydrogen chloride, the 2,4,6-tribromoaniline was precipitated in the form of the hydrochloride, which on recrystallization from alcohol gave up its hydrochloric acid and the free 2,4,6-tribromoaniline was then identified by its physical properties and analysis.

This reaction between bromine and 3,5-dibromo-4-aminobenzhydrol may be expressed in this way:

$$\begin{array}{l} C_6H_5—CH(O\vdots H)—C_6H_2Br_2NH_2 \longrightarrow C_6H_5CHO + C_6H_2Br_3NH_2 + HBr. \\ \qquad\qquad\qquad\ \vdots Br\ \ Br \end{array}$$

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[1] The proof of the positions of these two atoms of bromine is given later in this paper.

The mechanism of the reaction may be that the hydrol is first split into tribromaniline and bromphenylhydroxymethane which last breaks down into benzaldehyde and hydrobromic acid, thus:

$$C_6H_5CH(OH)Br + C_6H_2Br_3NH_2 \longrightarrow C_6H_5CH{:}O + HBr$$

The fact that tribromoaniline is obtained, with bromine atoms arranged on each side of the NH_2 group, proves the bromine atoms in the original dibromo-4-aminobenzhydrol to have been in the 3,5-positions.

We shall study the reaction further and shall extend our investigations to other derivatives of benzhydrol, to see if this reaction is a general one.

Experimental Part.

Preparation of p-Aminobenzophenone.—The first of the *p*-aminobenzophenone used in this work was made by the following process: Phenylbenzoylamide was formed by heating together aniline and benzoyl chloride according to the method of Gerhardt.[1] This has the formula

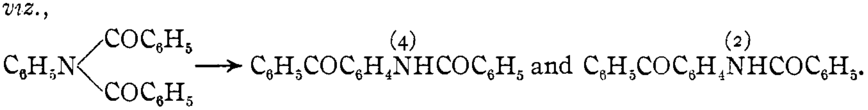
$$C_6H_5—NH—COC_6H_5.$$

On heating with benzoyl chloride and anhydrous zinc chloride this formed benzoyl-*p*-aminobenzophenone,[2]

$$C_6H_5—CO—C_6H_4NH—CO—C_6H_5.$$

By boiling the last with alcoholic soda, it was saponified, giving *p*-aminobenzophenone and sodium benzoate.

In the later work a new method has been devised for the preparation of *p*-aminobenzophenone, which was suggested by the work of Chattaway,[3] who showed that when dibenzanilide was heated with anhydrous zinc chloride at 220–230° for twenty hours, a rearrangement took place, *viz.*,



$$C_6H_5N\begin{cases}COC_6H_5\\COC_6H_5\end{cases} \longrightarrow C_6H_5COC_6H_4\overset{(4)}{N}HCOC_6H_5 \text{ and } C_6H_5COC_6H_4\overset{(2)}{N}HCOC_6H_5.$$

The scheme in brief for this new method of preparing *p*-aminobenzophenone consists in first allowing two molecules of benzoyl chloride to act on one molecule of aniline at 170–180° for a few moments, forming benzanilide together with a small amount of dibenzanilide, then, by the addition of anhydrous zinc chloride and the raising of the temperature to 200°, the remaining benzoyl chloride tends to substitute in the ring rather than in the amino group and whatever dibenzanilide has been already formed will tend to rearrange as indicated by Chattaway,[4] giving benzoyl *p*-aminobenzophenone which can then be saponified.

This was actually carried out in the manner of the following experiment:

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[1] *Ann.*, 60, 31.

[2] Higgin, *J. Chem. Soc.*, 41, 133.

[3] *J. Chem. Soc.*, 85, 394.

[4] *Loc. cit.*

To 100 grams of aniline contained in a two-liter flask, fitted with an air condenser, 330 grams (a slight excess above two molecules) of benzoyl chloride were slowly added from a dropping funnel, and the mixture heated in an oil bath for fifteen minutes at 170–180°, when 5 grams of pulverized, anhydrous zinc chloride were introduced and at the same time the temperature was increased to 200–210°. The oil bath was maintained at this temperature for ten hours, while every two hours 3 grams of pulverized anhydrous zinc chloride were added. At the end of this time the hot liquid was poured out into an enameled iron dish, where it cooled and solidified and was later recrystallized from alcohol. This process ran very smoothly and the reaction mixture was practically free from charring. After twice recrystallizing from alcohol, the benzoyl *p*-aminobenzophenone was white and ready for saponification. The yield was in various experiments from 85–90 grams.

In saponifying the benzoyl *p*-aminobenzophenone the method of Döbner[1] was used, namely, boiling with alcoholic soda. For every 10 grams of benzoyl *p*-aminobenzophenone 2 grams of ordinary sodium hydroxide were used. The sodium hydroxide was dissolved in 12.5 cc. of water and added to the benzoyl-*p*-aminobenzophenone dissolved in 43 cc. of hot alcohol. The solution was refluxed on a steam bath for seven hours, and water added hot, just to turbidity. On cooling, *p*-aminobenzophenone separated out in feathery crystals and was purified either by crystallizing from carbon tetrachloride or by dissolving in hot alcohol and adding hot water just to turbidity and allowing to cool. The yield was 90–95 per cent. of the theoretical.

3,5-Dibromo-4-aminobenzophenone.—For the preparation of this compound in a typical experiment 10 grams of *p*-aminobenzophenone were dissolved in 100 cc. of dry chloroform (which had been washed three times with distilled water and dried carefully with calcium chloride) and to the solution four atoms—that is, 16.2 grams—of bromine were added, and the whole heated with a return condenser for two hours. During the boiling, hydrobromic acid vapors were given off, but at the end of two hours the evolution of these had ceased, and a perfectly clear solution had resulted. The chloroform was evaporated on the steam bath and left a dark colored, crystalline residue which recrystallized readily from alcohol or glacial acetic acid, and less satisfactorily from much naphtha or a little chloroform. It was actually recrystallized once from alcohol, once from naphtha and six times from alcohol, and was then in the form of fine white needles, melting at 146°.

Calculated for $C_{13}H_9ONBr_2$: Br, 45.05; found, 45.04.

Properties: When recrystallized from alcohol, fine white needles. From naphtha, when allowed to crystallize slowly, long, flat, narrow

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[1] *Ann.*, 210, 271.

plates. Melting point, 146°. It is soluble in acetone, benzene, hot alcohol, chloroform, hot glacial acetic acid, and carbon tetrachloride. Insoluble in water and practically so in cold naphtha. Concentrated hydrochloric acid in a sealed tube at 105–110° for five hours is without action.

3,5-Dibromo-4-aminobenzhydrol.—This was produced from 3,5-dibromo-4-aminobenzophenone by reduction with aluminum amalgam—sodium amalgam having been found to remove the halogen from the ring.

The benzophenone was dissolved in a mixture of 30 parts by weight of hot alcohol and 10 of hot water and to the solution the aluminum amalgam from roughly 20 grams of aluminum were added and the whole heated on the steam bath. At the end of an hour and a half, the hot liquid was decanted from the mercury, filtered from the aluminum hydroxide, and cooled, when white needles precipitated, which were removed by filtration and pressed out on a porous plate. The needles were recrystallized, twice from chloroform and three times from alcohol, until the constant melting point, 147.5°, was reached.

Calculated for $C_{13}H_{11}ONBr_2$: Br, 44.79; found, 44.72.

Properties: This substance crystallizes in white needles, melting at 147.5°. It is soluble in ether, acetone and much naphtha. Soluble also in hot benzene, hot carbon tetrachloride and hot glacial acetic acid. Insoluble in water.

Action of Bromine on 3,5-Dibrom-4-aminobenzhydrol.—For the purpose of examining the action of bromine on the 3,5-dibromo-4-aminobenzhydrol, the latter substance was dissolved in twenty parts by weight of dry chloroform (which had been (previous to drying) thoroughly washed out with water) by warming on the steam bath. A slight excess over two atoms of bromine was then added. The bromine color very soon disappeared, whereupon the solution was cooled quickly down to room temperature and dry hydrochloric acid gas passed in. A yellowish crystalline precipitate formed and was quickly filtered off. The chloroform filtrate was evaporated, leaving a residual oil which had the odor and characteristics of benzaldehyde, but since the quantity was not large, a boiling point was not taken but, instead, it was converted into its hydrazone by dissolving in ether and adding a sufficient quantity of freshly distilled phenylhydrazine. The white precipitate thus produced was crystallized from alcohol, and then melted at 153.5–154°, thus corresponding to the phenylhydrazone of benzaldehyde, the melting point of which is given by Behrend and Leuchs,[1] as 156°. The other properties of our compound were coincident with those of the phenylhydrazone of benzaldehyde.

The yellow crystalline precipitate mentioned above as thrown down from the chloroform solution when dry hydrogen chloride was passed in was

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[1] *Ann.*, 257, 227.

the hydrochloride of 2,4,6-tribromoaniline. It was recrystallized three times from alcohol (thereby of course losing its added molecule of hydrochloric acid) and then melted at 119°, and showed the other properties of 2,4,6-tribromoaniline.

Calculated for $C_6H_4NBr_3$: Br, 72.71; found, 73.11.

The action of bromine was tried on 3,5-dibromo-4-aminobenzophenone in certain preliminary studies which will be continued. No splitting apart of the two benzene nuclei takes place as with the corresponding hydrol, but perbromide bodies are formed.

This research will be continued in this laboratory and extended to other benzhydrol derivatives.

CAMBRIDGE, MASS.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 69.]

THE ELECTRON CONCEPTION OF VALENCE. II. THE ORGANIC ACIDS.

BY K. GEORGE FALK.

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1. Introduction. 2. Theoretical Considerations. 3. Saturated Monobasic Acids. 4. Saturated Dibasic Acids. 5. Unsaturated Acids. 6. Aromatic Acids. 7. Summary.

1. Introduction.—The hypothesis of Sir J. J. Thomson, according to which the linkages or bonds between the atoms in a molecule are formed by the transfer of corpuscles, was developed mainly in relation to organic compounds in a preceding article.[1] It will be applied in this paper to the ionization relations of organic acids. The ionization constants ($K \times 10^5$) of the acids as calculated from the Ostwald dilution law, $K = \frac{\gamma^2}{v(1-\gamma)}$, in which v = the volume in cubic centimeters containing one mol of the acid, and γ = the degree of ionization found from the conductance ratio, will be used. The factors upon which the accuracy and reliability of K depend for any one acid at a definit temperature for a series of concentrations have been discussed in detail by Scudder.[2] Only those acids will be considered for which a fairly reliable value of K has been obtained. This eliminates the highly ionized acids for which K varies with change in concentration. The data refer to 25° and the results of a number of different observers have been used.[3]

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[1] Falk and Nelson, THIS JOURNAL, **32**, 1637–54 (1910).

[2] *J. Physic. Chem.*, **7**, 293 (1903).

[3] Ostwald, *Z. physik. Chem.*, 3, 170, 241, 369 (1889). Bethman, *Ibid.*, **5**, 385 (1890). Berthelot, *Ann. chim. phys.*, [6], 23, 43 (1891). Crum Brown and Walker, *Ann.*, **261**, 116 (1891). Walker, *J. Chem. Soc.*, **61**, 696 (1892). Walden, *Z. physik. Chem.*, 8, 448 (1891); 10, 646 (1892). Stohmann and Kleber, *J. prakt. Chem.*, **45**, 480