minutes, liquefaction is complete throughout the mass. These operations can, of course, be repeated indefinitely.

The conditions here seem analogous to those which obtain between calcium oxide, carbon dioxide and calcium carbonate at a temperature in the vicinity of 800°. As the action in the present case is so rapid, and can be so readily followed by the eye, it is suggested that the experiments just described might well find use in demonstrating to students this particular application of the "phase rule."

A rough measurement of the difference in level of the mercury in bulbs D and E, when both solid and liquid are present in B, shows that the dissociation pressure of the addition product is somewhere in the vicinity of 500 mm. This is but a rough approximation. An accurate measurement has not yet been attempted, as in the experiments hitherto made I could not be certain that the hydrogen chloride was free from air. Another form of apparatus has been designed to meet this difficulty, and when the work is resumed in the autumn, more accurate measurements will be made. The question whether the addition-product is a chemical compound or a solution will then be taken up, and the investigation extended to the action of hydrogen bromide and iodide as well as other compounds upon piperonal.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY,
BOSTON, MASS.
June 5, 1906.

BENZOYL-p-BROMPHENYLUREA: A BY-PRODUCT IN THE PREPARATION OF BENZBROMAMIDE.

BY F. J. MOORE AND A. M. CEDERHOLM.

Received June 7, 1906.

IN 1882, Hofmann,[1] while carrying on his celebrated investigation of the action of bromine and alkali upon amides, discovered acetbromamide. At the same time he made the observation that this substance reacts both with aniline and with phenol to form tribromaniline and tribromphenol respectively—acetamide being regenerated in accordance with the following equation.

$$C_6H_5.NH_2 + 3C_6H_5—CO.NHBr = C_6H_2(Br_3)NH_2 + 3C_6H_5CO.NH_2.$$

The chemical behavior of acetbromamide and analogous compounds has since been investigated by Seliwanow[2] and others,

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[1] Ber. 15, 410 (1882).

[2] Ibid. 26, 424 (1893).

but the use of benzbromamide as a brominating agent seems not to have been adequately studied. An extended investigation of the subject is now being carried on in this laboratory. The results will be communicated later by one of us in connection with another collaborator. It is sufficient to say here that the products are not infrequently different from those obtained when bromine is employed.

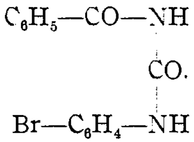
The occasion of the present investigation was an observation made while studying the action of benzbromamide upon phenol. If these substances are allowed to react in ethereal solution, the following apparent metathesis occurs, fully analogous to that observed by Hofmann.

$$C_6H_5OH + 3C_6H_5.CO.NHBr = C_6H_2(Br_3)OH + 3C_6H_5\text{—}CONH_2.$$

Mixed with the tribromphenol and the benzamide, however, there appeared another substance whose presence was, at first, not so easy to explain.

Properties of the By-product.—This substance is a white solid, insoluble in hot and cold water, and in cold dilute alkali, but soluble in cold concentrated sulphuric acid. It is insoluble in ether, but when boiled with large quantities of alcohol, benzene, or chloroform, it dissolves, and crystallizes from each of these solvents in extremely fine silky needles. It is somewhat more soluble in glacial acetic acid, and the crystals obtained from this solvent are a little more compact. When heated in a melting-point tube of the ordinary form, the substance decomposes in the vicinity of 227°, with the formation of a reddish brown sublimate. If the melting-point tube be sealed off at the top before the determination is made, the substance melts quite sharply at 230°, and decomposes 2° higher. These phenomena are very characteristic. The substance contains both nitrogen and bromine. It was at first supposed that it might be a product of the action of benzbromamide upon phenol, but it soon became evident that the new substance existed as an impurity in the benzbromamide employed. From the latter it is easy to separate on account of its insolubility in cold dilute sodium hydroxide. When the impure benzbromamide is washed with this reagent, a white residue is obtained. This contains the by-product together with some benzamide. The latter is readily removed by treatment with boiling water, which dissolves the benzamide.

Constitution.—The investigation had reached this point when our attention was called to a paper by Stieglitz and Earle[1] who prepared benzoyl-*p*-chlorphenylurea by the action of phenyl isocyanate upon benzchloramide, among other methods. The properties of the compound we were studying led us to suspect that it was the analogous bromine compound—benzoyl-*p*-bromphenylurea,



$$\begin{array}{r} C_6H_5{-}CO{-}NH \\ \vert\;\; \\ CO.\, \\ \vert\;\; \\ Br{-}C_6H_4{-}NH \end{array}$$

This view was supported by the following analysis:

	Calculated for $C_{14}H_{11}O_2N_2Br$. Molecular weight, 319.1.	Found.	
		I.	II.
C	52.65	52.73	......
H	3.47	3.50	......
O	10.02	......	......
N	8.80	9.21	......
Br	25.06	25.08	24.98

Syntheses.—As no description of a benzoylbromphenylurea was found in the literature, we were under the necessity of proving the constitution of the substance by synthetic methods. This was accomplished by means of reactions for the most part similar to those employed by Stieglitz and Earle in their study of the chlorine compound. One of these reactions, that of benzoyl chloride upon *p*-chlorphenylurea, was not available, as Pinnow[2] has studied the action of benzoyl chloride upon *p*-bromphenylurea, and found that it proceeds in a different sense, yielding benzonitrile and benzoyl-*p*-bromanilide. As the preparation of *p*-bromphenylurea itself offers some difficulties, it did not seem worth while to repeat this work on the chance of there being another product which Pinnow might have overlooked. This seemed all the more unnecessary as we were able to prepare the compound in four other ways: (1) by the action of phenyl isocyanate upon benzbromamide in benzene solution; (2) by the action of *p*-bromphenyl isocyanate upon benzbromamide in alkaline solution; (3) by the action of *p*-bromphenyl isocyanate upon benzamide when these substances are heated together; (4)

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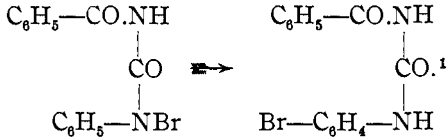
[1] Am. Ch. J. 30, 412 (1903).

[2] Ber. 24, 4172 (1891).

by the action of benzbromamide upon benzoylphenylurea in benzene solution. These syntheses leave no room for doubt that the compound has the constitution already indicated.

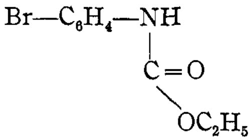
(1) *Preparation from Phenyl Isocyanate and Benzbromamide.*—For this experiment a specially prepared and purified sample of benzbromamide was employed which was completely soluble in cold dilute sodium hydroxide, and hence could have contained no appreciable quantity of the by-product under consideration. This material was used in all subsequent synthetic experiments where benzbromamide was required. Two grams of the pure benzbromamide were heated with 1.5 grams phenyl isocyanate and 5 cc. benzene on the water-bath. At 90° all went into solution, the mixture becoming deep red in color. Soon after, a bulky white precipitate appeared, and the supernatant liquid became nearly colorless. The precipitate was filtered off, washed with alcohol, dried and recrystallized from chloroform. The crystals thus obtained melted at 227° with decomposition, and when mixed with some of the by-product obtained from the impure benzbromamide, did not depress its melting-point. The yield was nearly quantitative. The reaction is as follows:

$C_6H_5\text{—}N=C=O+C_6H_5\text{—}CO.NHBr=$



$$\begin{array}{c} C_6H_5\text{—}CO.NH \\ | \\ CO \\ | \\ C_6H_5\text{—}NBr \end{array} \longrightarrow \begin{array}{c} C_6H_5\text{—}CO.NH \\ | \\ CO. \\ | \\ Br\text{—}C_6H_4\text{—}NH \end{array}$$ [1]

(2) *Preparation from p-Bromphenylurea and Benzbromamide.*—Some difficulty was experienced in preparing the *p*-bromphenyl isocyanate for use in this and the following synthesis. At first we followed the directions of Dennstedt[2] who treated *p*-bromphenyl urethane with phosphorus pentoxide in accordance with the following reaction:



$$\begin{array}{l} Br\text{—}C_6H_4\text{—}NH \\ \qquad\qquad\quad | \\ \qquad\qquad\quad C=O \\ \qquad\qquad\quad \diagdown \\ \qquad\qquad\qquad OC_2H_5 \end{array} =H_2O+C_2H_4+Br\text{—}C_6H_4\text{—}N=C=O.$$

Dennstedt states that the product can be distilled off from the

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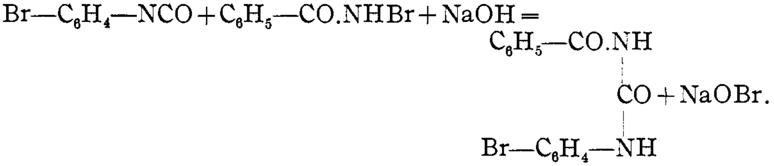
[1] The wandering of the halogen atom has been discussed by Stieglitz and Earle.

[2] Ber. 13, 228 (1880).

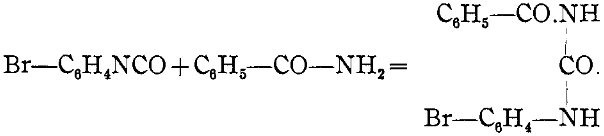
reaction mixture. In our experiments decomposition always sets in when distillation was attempted. The conditions were varied, but with no better result, and extensive decomposition was observed even when the heating was done in a bath, and the distillation conducted in vacuum. A little of the isocyanate sought could usually be identified in the distillate, but the quantity was utterly insufficient for use in further work. Attempts to distil were therefore abandoned, and the reaction mixture extracted with ligroin instead. In this way a yield of about 30 per cent. was obtained.

Four-tenths gram of the isocyanate was intimately mixed with one molecule of pure benzbromamide, and one molecule of sodium hydroxide added in the form of a 10 per cent. solution. The mixture was thoroughly shaken for twenty minutes, and then filtered. The precipitate was washed with water and then with cold alcohol. Finally it was recrystallized from hot alcohol. A melting-point comparison made as in previous cases, showed that this substance was identical with the by-product studied.



$$\mathrm{Br—C_6H_4—NCO + C_6H_5—CO.NHBr + NaOH =} \begin{array}{r} \mathrm{C_6H_5—CO.NH} \\ | \\ \mathrm{CO} \\ | \\ \mathrm{Br—C_6H_4—NH} \end{array} \mathrm{+ NaOBr.}$$

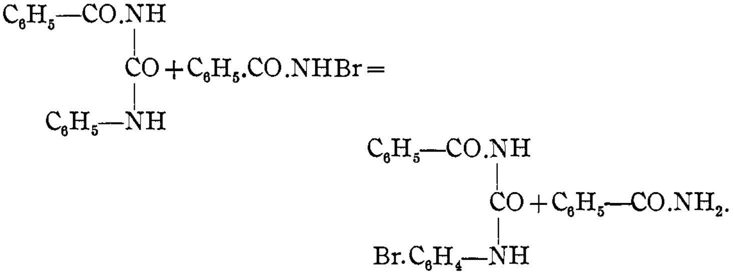
(3) *Preparation from p-Bromphenyl Isocyanate and Benzamide.*—Two-tenths gram of the isocyanate (one molecule) was intimately mixed with benzamide (one molecule) and the mixture heated in an oil-bath at 175°—thermometer in bath. An odor suggestive of bitter almonds was noticed during the heating. The dark colored reaction product was treated with hot water to dissolve benzamide, and the residue washed first with alcohol, and then with chloroform, and finally crystallized from the latter solvent. The yield was small, but the product could be identified with the benzoyl-*p*-bromphenylurea produced by other methods.



$$\mathrm{Br—C_6H_4NCO + C_6H_5—CO—NH_2 =} \begin{array}{r} \mathrm{C_6H_5—CO.NH} \\ | \\ \mathrm{CO.} \\ | \\ \mathrm{Br—C_6H_4—NH} \end{array}$$

(4) *Benzoylphenyl from Benzoylphenylurea and Benzbromamide.*—Benzoylphenylurea was prepared according to the method of

Kühn[1] by the action of phenyl isocyanate upon benzamide. The preparation presents no difficulties. 0.25 gram of the product was heated with 0.21 gram benzbromamide in benzene solution for about twenty minutes. On cooling, a bulky white precipitate appeared. This was washed with boiling water and finally recrystallized from chloroform. The usual melting-point tests showed it to be benzoyl-*p*-bromphenylurea which must have been formed by the following reaction:



$$\begin{array}{l} C_6H_5—CO.NH \\ \qquad\qquad | \\ \qquad\qquad CO \\ \qquad\qquad | \\ \quad C_6H_5—NH \end{array} + C_6H_5.CO.NHBr = \begin{array}{l} C_6H_5—CO.NH \\ \qquad\qquad | \\ \qquad\qquad CO \\ \qquad\qquad | \\ Br.C_6H_4—NH \end{array} + C_6H_5—CO.NH_2.$$

HOW THE BY-PRODUCT IS FORMED.

Preparation of the Benzbromamide.—To three molecules of sodium hydroxide in 33 per cent. solution was added two atoms of bromine with constant shaking, the flask being surrounded by ice water, and pieces of ice also being added from time to time to the reaction mixture. As soon as all the bromine had been dissolved, one molecule of finely ground benzamide was added with the same precautions. Some of the benzamide usually remained undissolved. This was removed by rapid filtration with the aid of suction, broken ice being placed in the filter bottle to keep the filtrate cold. To this filtrate, dilute, ice-cold acetic acid was added as long as a precipitate formed. At this point a red color was observed and the solution smelled strongly of bromine. This must have come from the reaction of the acid upon some hypobromite or bromate present in the solution along with the excess of sodium bromide. The precipitate was then filtered off, freed as much as possible from the mother-liquor by suction, and dried on porous plates. It was usually left spread out on these over night, and then crystallized from boiling benzene. Two crystallizations were usually necessary to secure a colorless product. The crystals thus obtained were flaky in structure, and the forms were not well marked.

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[1] Ber. 17, 2880 (1884).

It will be observed that the method just described closely follows the directions of Hoogewerff and Van Dorp[1] also recommended by Hantzsch.[2] It differs in the use of sodium instead of potassium hydroxide and also in the use of an alkali solution which was more concentrated at the beginning of the reaction. As ice was added freely while the reaction progressed, the solution was probably as dilute at the end of the reaction as in the experiments of Hoogewerff and Van Dorp.

In our first experiments, about 50 grams of benzamide were used for each preparation. Later, when it became necessary to prepare especially pure material, only 10 grams were used, and about the same routine followed, except that additional pains were taken to perform all operations as slowly and at as low a temperature as possible. The substance prepared in this way crystallized in lustrous plates and was entirely soluble in cold dilute sodium hydroxide.

The impure product first described showed a tendency to grow reddish in color on standing, and emitted an odor resembling that of bromine. This led us to think that the formation of the brominated urea might be traced to a spontaneous decomposition of the benzbromamide, either while drying in contact with the dilute acetic acid or in the benzene solution during the process of crystallization, or, finally, by standing in the bottle. Various experiments were made to test these points, the details of which need not be given here. The crystalline impure benzbromamide was allowed to stand at various temperatures, both dry and in the presence of dilute acetic acid; it was also boiled with a return condenser for varying lengths of time both in benzene and in toluene solution. In none of these cases was it apparent that the amount of benzoyl-*p*-bromphenylurea in the product had perceptibly increased. The cause of its formation had, therefore, to be looked for at some earlier stage.

CONCLUSION.

We finally concluded that the key to the solution of this problem was to be found in an observation of Van Dam and Aberson.[3] These investigators found that a dilute solution of the potassium salt of benzbromamide decomposes with the formation of benzoyl-

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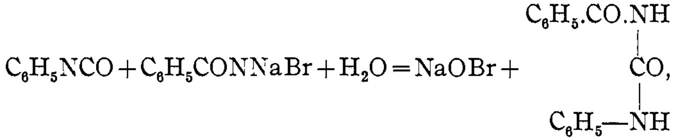
[1] Rec. trav. chim. 8, 188 (1889).

[2] Ann. 296, 86 (1897).

[3] Rec. trav. chim. 19, 318 (1900).

phenylurea, and further that the reaction proceeds more rapidly in this sense, the more nearly neutral the solution. This behavior can be represented by the following equations, assuming the presence of some phenyl isocyanate at this point, (this would be in harmony with the views of most students of Hofmann's reaction):

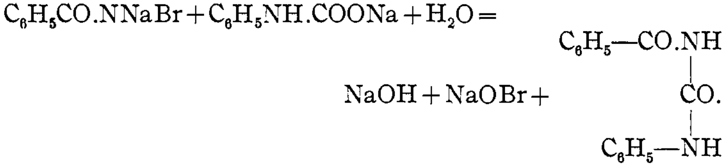
(1) $$C_6H_5—CONNaBr = NaBr + C_6H_5NCO.$$

(2) 

$$C_6H_5NCO + C_6H_5CONNaBr + H_2O = NaOBr + \begin{array}{r} C_6H_5.CO.NH \\ | \\ CO, \\ | \\ C_6H_5—NH \end{array}$$

or if with E. Mohr,[1] sodium phenylcarbamate is assumed as an intermediate product,

(1) $$C_6H_5.CO.NNaBr + NaOH = NaBr + C_6H_5—NH.COONa.$$

(2) 

$$C_6H_5CO.NNaBr + C_6H_5NH.COONa + H_2O = NaOH + NaOBr + \begin{array}{r} C_6H_5—CO.NH \\ | \\ CO. \\ | \\ C_6H_5—NH \end{array}$$

In the preparation of benzbromamide, when the acetic acid is added, the neutral solution favorable for these reactions is produced, and the precipitate consists of a mixture of benzbromamide and benzoylphenylurea. When this mixture is crystallized from benzene, the latter is brominated by the former in accordance with the reactions described in the fourth synthesis mentioned above. In fact this synthesis was originally carried out to test this very point.

Another possibility has to be considered. It has been already noted that when the acetic acid is added, some bromine seems to be liberated. This might effect the bromination. We are inclined to reject this hypothesis, partly because the last synthesis just alluded to has shown that the benzbromamide can accomplish this result, partly because Van Dam and Aberson and other investigators have only observed the non-brominated product, and partly because where the brominated urea has been met with, it has been accompanied by benzamide. The presence of the latter can be most easily accounted for on the assumption that

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[1] J. pr. Chem. [2] 73, 177 (1906).

benzbromamide is the brominating agent. Furthermore, it is not easy to see why a substance as insoluble as benzoylphenylurea should be much affected by dilute bromine water.

The improvement in the quality of benzbromamide when only small quantities were prepared, is doubtless to be explained by the fact that, under these circumstances, it is easier to maintain a low temperature throughout, less of the benzbromamide being decomposed to form isocyanate or carbamate.

SUMMARY.

When benzbromamide is prepared by the method of Hoogewerff and Van Dorp, it is liable to contain benzoyl-*p*-bromphenylurea. The amount of this substance may sometimes exceed 10 per cent.

Benzoyl-*p*-bromphenylurea is a bulky, colorless, crystalline solid. It melts in a closed tube at 230° and decomposes at 232°. It is soluble with difficulty in most of the ordinary organic solvents.

The constitution assigned to this compound is most conclusively proved by its synthesis from *p*-bromphenyl isocyanate and benzamide, but it is also consistent with its preparation by three other syntheses, with the analysis, and with its whole behavior.

The formation of the benzoyl-*p*-bromphenylurea in the preparation of benzbromamide is to be accounted for as the result of the bromination of the benzoylphenylurea first formed. This bromination is probably effected by the benzbromamide itself.

The authors perform a pleasant duty in acknowledging their indebtedness to Dr. Richard B. Earle, instructor in organic chemistry at the institute, for many helpful suggestions.

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NOTES ON SOME OF THE CONIFER OILS.

BY R. E. HANSON AND E. N. BABCOCK.

Received June 20, 1906.

AN apparent want of conformity in the present literature on some of the conifer oils has led us to investigate several of them, and we hereby embody the results of our work.

Our investigation has been confined to the following oils: