

Only a little nitrile was obtained. In Expt. 2 the lower layer of the distillate was passed through the apparatus again, but only a small additional amount of nitrile was produced.

It appears from Table II that most of the nitrile is found in the upper layer and, when 100% acid is used, a good yield of the nitrile is obtained even when the lower layer is discarded. As we would expect, in the experiments with weaker acid, particularly the 70% acid, a larger amount, in some cases, half or more of the nitrile, is found in the lower layer.

It is intended to continue this work, particularly with the study of the formation of other nitriles.

Summary.

1. It is found that acetic acid vapor, mixed with a moderate excess of ammonia and passed over alumina or thoria at 500°, gives a large yield, up to 85%, of acetonitrile.

2. This reaction does not take place in case the catalyst is omitted.

3. The yield depends on the activity of the catalyst and may vary greatly for what appear to be trifling differences in the method of preparation of the catalyst.

4. So far as the present work goes, alumina appears to be the best catalyst and about 500° the best working temperature.

5. This method of preparation of acetonitrile is a continuous process requiring very little attention, and is adapted to use for the preparation of large quantities.

BALTIMORE, MD.

[CONTRIBUTIONS FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON AMINES. V. THE STRUCTURE OF VITIATINE. SYNTHESIS OF METHYLETHYLENEDIAMINE.¹

BY TREAT B. JOHNSON AND GEORGE C. BAILEY.

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The only compound conforming in constitution to the expression $C_5H_{14}N_6$, that is recorded in Richter's *Lexikon der Kohlenstoffverbindungen* is the base *Vitiatine* whose structure has never been established. This interesting substance was isolated by Kutscher² from beef extract by precipitation in the form of its gold salt, which gave analytical values agreeing with that calculated for $C_5H_{14}N_6 \cdot 2HCl \cdot 2AuCl_3$. Later, during a careful investigation of the nature of the toxic bases in urine, Kutscher³ identified the same amine and ascribed its origin, in this case to the metab-

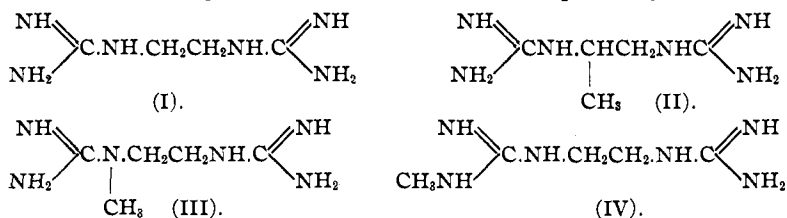
¹ This paper was constructed from a Dissertation presented by Mr. George Corbin Bailey to the Faculty of the Graduate School of Yale University, 1916, in candidacy for the Degree of Doctor of Philosophy.

² *Zentr. Physiol.*, **21**, 33 (1907).

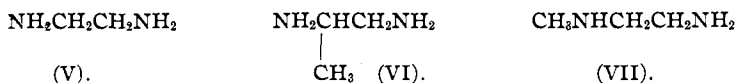
³ *Z. physiol. Chem.*, **51**, 457 (1907).

olism of flesh food. The following year Engeland duplicated this work of Kutscher's and confirmed his original observations by isolating the same substance in the form of its gold salt from beef extract and urine.¹ Kutscher obtained no chemical evidence upon which to base a structural formula, but assigned to the amine, however, the provisional Formula III, to show its possible relationship to the other bases found with it in urine, *viz.*, guanidine, methylguanidine, dimethylguanidine and creatine.

If *vitiatine* is to be considered as a *mono*-methyl derivative of ethylene-guanidine² (I) there are just three structural formulas to which it can theoretically conform, namely: the carbon-substituted derivative represented by Formula II, and the two isomeric nitrogen-substituted compounds corresponding to Formulas III and IV, respectively.



None of these have been prepared. The structure of all three combinations (II, III and IV) would be established by their behavior on hydrolysis. The combinations (II) and (IV) would be productive of diaminopropane³ (VI) and ethylenediamine (V), respectively, with formation of ammonia and monomethylamine, while a compound having the structure assigned to *vitiatine* (III) would give four proportions of ammonia and monomethylethylenediamine. In other words, the basic nucleus of *vitiatine*, if Kutscher's formula is correct, is the monomethylated base (VII), which has not been described in the literature. The primary object of this investigation was to develop a method of synthesizing this unknown amine.



A successful method of synthesizing this compound (VII) was not developed until after we had considered and tried, without success, a number of different methods which seemed feasible of application. No attempts were made by us to prepare the methyl derivative from ethylenediamine by direct alkylation, because Schneider⁴ has already shown that this base undergoes exhaustive alkylation by treatment with methyl iodide giving the diquaternary salt $1(\text{CH}_3)_3\text{N} \cdot \text{CH}_2 \text{CH}_2 \text{N}(\text{CH}_3)_3\text{I}$. The

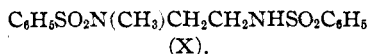
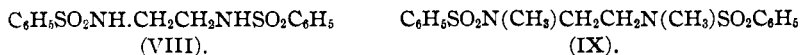
¹ *Z. untersuch. Nahr. und Genussm.*, 16, 658 (1909); *Z. physiol. Chem.*, 57, 49 (1908).

³ This simple guanidine has never been synthesized.

² Hoffmann, *Ber.*, 6, 308 (1873).

⁴ *Ber.*, 28, 3073 (1895).

synthesis of the symmetrical dimethyl derivative was accomplished by Schneider by alkylation of the phenylsulfonamide (VIII) with methyl iodide and then hydrolyzing the resulting dialkyl derivative (IX), with hydrochloric acid. He did not succeed in obtaining by alkylation the monomethyl derivative of the sulfonamide (X). We have applied a

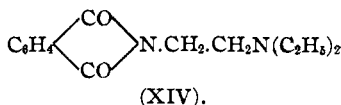
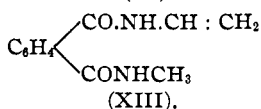
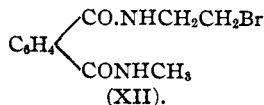
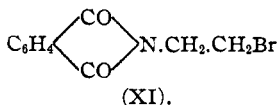


similar reaction with the dibenzylsulfon derivative of ethylenediamine,



and have succeeded in isolating, after alkylation, both the corresponding dimethyl and methyl derivatives. The yield of the latter, however, was so small that the synthesis was of no practical value for the preparation of the free amine. The application of Mendius' reaction was considered by us and the nitrile of sarcosine $\text{CH}_3\text{NHCH}_2\text{CN}$ ¹ and the corresponding phenylsulfon derivative, $\text{C}_6\text{H}_5\text{SO}_2\text{N}\cdot(\text{CH}_3)\cdot\text{CH}_2\text{CN}$,² were reduced with sodium and alcohol, but in neither case was the operation productive of combinations from which we were able to separate the methylethylenediamine (XII). The action of ammonia on bromoethylmethylamine, $\text{CH}_3\text{NHCH}_2\text{CH}_2\text{Br}$, and the corresponding chlorine compound was not investigated. Marckwald and Frobenius,³ who prepared these amines, have shown that they interact abnormally with alkalis with formation of the cyclicimide, $\text{CH}_2\cdot\text{CH}_2\cdot\text{N}\cdot\text{CH}_3$. Bromoethylphthalimide (XI),

also shows irregularities in its behavior towards amines. Ristenpart⁴ attempted to prepare the phthalyl derivative of methylethylenediamine by heating this bromide with methylamine, but found, contrary to his expectation, that they interacted in an entirely different manner giving a mixture of the bromoamide (XII), and the corresponding vinyl derivative represented by Formula XIII. Diethylamine, on the other hand, reacted normally with formation of the diamino combination (XIV), but the yield was poor.



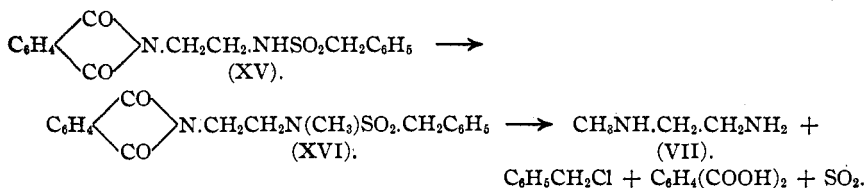
¹ Eschweiler, *Ann.*, **279**, 40 (1894).

² Johnson and McCollum, *Am. Chem. J.*, **35**, 59 (1906).

³ *Ber.*, **34**, 3544 (1901).

⁴ *Ibid.*, **29**, 2526 (1896).

The synthesis of methylethylenediamine (VII), has now been accomplished by a method which involves the use of bromoethylphthalimide. We find that this halide interacts with the potassium salt of benzylsulfonamide giving the corresponding acid amide (XV). This undergoes alkylation smoothly with methyl iodide, forming the methyl derivative (XVI), which gives on hydrolysis with hydrochloric acid the amine (VII), phthalic acid, sulfur dioxide and benzyl chloride. The transformation is a quan-



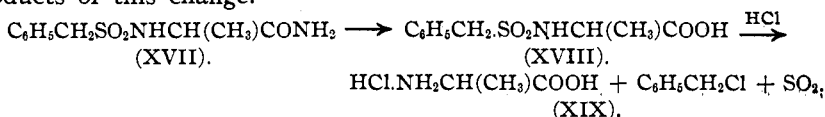
titative one with the exception of the first phase involving the formation of the amide (XV). The first attempts to prepare this were made by allowing the potassium salt of benzylsulfonamide to react with bromoethylphthalimide in alcohol. This method proved a failure as the bromide was decomposed by the alkali with displacement of the halogen by hydroxyl and production of β -hydroxyethylphthalimide.¹ Phenylsulfonamide was tried in place of benzylsulfonamide with the same result. Modifications in procedure were made by changing the strength of alcohol used and varying the time of heating; catalytic agents were introduced and the operation of preparing the salt of the sulfonamide was modified, but in no case was the desired combination formed. Attempts were then made to bring about the change by digesting the bromide with the potassium salt of the amide in benzene, toluene and petroleum ether but no reaction took place under such conditions. Formation of the amide was finally accomplished by fusing the dry potassium salt with bromoethylphthalimide. The best yield, however, that could be obtained by this procedure was 40% of the theoretical. The potassium salt of phenylsulfonamide interacts with bromoethylphthalimide under similar conditions, giving the corresponding phenylsulfonamide (see experimental part).

In the course of our work we had occasion to investigate the behavior on hydrolysis of several alkyl derivatives of benzylsulfonamide. In every case examined, such combinations always broke down when heated with hydrochloric acid with complete destruction of the sulfonic acid. The hydrolysis generally takes place quantitatively below 140°, and by evaporation of the resulting solution the hydrochloride of the amine is obtained free from sulfur compounds. Johnson and Ambler² utilized benzylsulfonamide in developing a synthesis of sarcosine. We have ap-

¹ Gabriel, *Ber.*, 21, 572 (1888).

² *THIS JOURNAL*, 36, 372 (1914).

plied their method of synthesis and prepared the amino acid—alanine. The potassium salt of benzyisulfonamide interacted smoothly with α -bromopropionamide in alcohol solution forming the corresponding sulfonamide (XVII). When this was digested with barium hydroxide in aqueous solution it was saponified smoothly with formation of the corresponding acid (XVIII). The latter was decomposed quantitatively when heated with hydrochloric acid at 130° , giving the hydrochloride of alanine (XIX). Benzyl chloride and sulfur dioxide were the secondary products of this change.



Our researches on amines will be continued.

Experimental Part.

The benzyisulfonchloride which was used in this investigation was prepared according to Pechmann's¹ directions by interaction of phosphorus pentachloride with the sodium salt of benzyisulfonic acid. This was converted into its corresponding amide, $\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{NH}_2$, but the action of ammonia.

Potassium Salt of Benzyisulfonamide, $\text{C}_6\text{H}_5\text{CH}_2\text{SO}_2\text{NHK}$.—This salt was prepared by dissolving a molecular proportion of potassium hydroxide in absolute alcohol and adding to the solution the required amount of the sulfonamide. After heating to boiling for one-half an hour the solution was cooled when the potassium salt separated in the form of micaceous flakes. The salt was separated by filtration and washed carefully with ether. For the success of the next operation this washing was essential in order to remove the mother liquor which contained traces of free alkali and unaltered amide. If dilute alcohol was used the salt separated in a more compact crystalline form and contained little free alkali. The salt did not melt below 300° . It was dried at 100° .

The Action of Bromoethylphthalimide on the Potassium Salt of Benzyisulfonamide: Phthalimidobenzyisulfonethylenediamine (XV).—In our preliminary work the potassium salt of benzyisulfonamide was prepared by dissolving 2.2 g. of potassium hydroxide in 40 cc. of alcohol and then dissolving 6.7 g. of the amide in the solution. After boiling for one-half an hour, 10 g. of bromoethylphthalimide were introduced and the solution finally digested until it gave no alkaline reaction. This operation requires from 2 to 3 hours. The precipitate which deposited was filtered off and the mother liquor evaporated to dryness. From the precipitate a theoretical yield of potassium bromide was obtained. The filtrate on evaporation left a yellow, gummy mass, which could not be

¹ *Ber.*, 6, 534 (1873).

crystallized from alcohol, water or ether. The substance became very viscous on warming and solidified to a gum in a freezing mixture. When the material was hydrolyzed in a bomb tube with hydrochloric acid, phthalic acid, benzyl chloride and benzylsulfonamide were formed and identified but no amine was obtained.

A number of experiments were afterwards made using modifications of the above, in which the time of heating, the quantity of alcohol and the strength of the alcohol were varied but without the desired results. It was found that the bromine atom of the phthalimide combination was replaced by a hydroxyl group in the alkaline solution and β -oxyethylphthalimide¹ was formed. The latter compound was isolated and identified by its melting point (126–127°). Similar results were obtained by the action of bromoethylphthalimide on an alcoholic solution of the potassium salt of phenylsulfonamide. In every experiment the sulfonamide was recovered unaltered. From these results it was concluded that bromoethylphthalimide cannot be used in alkaline alcoholic solution for such reactions. The above difficulties were finally partially overcome by working under the following conditions:

Molecular proportions of the potassium salt and bromoethylphthalimide were ground together in a mortar and the mixture heated in a flask at 100–110° for 4–5 hours. At the end of this time the melt was a black, viscous liquid which solidified on cooling. There was no reaction at 80° and no increase in yield was obtained by heating above 110° or longer than 5 hours. This residue was digested with water to remove potassium bromide. After filtering, the residue was subjected to the same treatment several times to remove the last trace of bromide and finally purified by digestion with 50% acetic acid in the presence of animal charcoal. On cooling, the ethylenediamine derivative separated and was further purified by recrystallization from glacial acetic acid. On concentrating the acetic acid filtrates more of the same product was obtained. Glacial or 50% acetic acid were the only solvents in which the compound could be digested with animal charcoal with removal of the coloring material.

From the water filtrate 80% of the theoretical quantity of potassium bromide was isolated, along with unaltered benzylsulfonamide and a low melting substance, which was identified as a mixture of bromoethylphthalimide and the sulfonamide.

The yield of phthalimidobenzylsulfonethylenediamine was 40% of theory. If alkali was present in the potassium salt used in its preparation this yield was decreased and more resinous material was obtained. The compound crystallized from acetic acid in slender prisms which melted at 175–176.5° to a clear oil. It is soluble in benzene, chloroform, methyl

¹ Gabriel, *Ber.*, 21, 572 (1888).

alcohol, ethyl alcohol and acetic acid; insoluble in water and slightly soluble in ether. It was dried for analysis at 100°.

Calc. for $C_{17}H_{16}O_4N_2S$: N, 8.14%. Found: N, 7.90, 8.2.

Before using this compound for methylation in the next experiment it was found advisable to crystallize it from alcohol, as there was a tendency for the amide to occlude acetic acid when crystallized from that solvent. Unless this was carefully removed unsatisfactory results were always obtained during alkylation, because the acid present interacted with the sodium alcoholate incorporated and a mixture of unaltered material and the methyl derivative obtained.

Alkylation of Phthalimidobenzylsulfonamide with Methyl Iodide. Phthalimidobenzylsulfonmethylethylenediamine (XVI).—Two grams of phthalimidobenzylsulfonethylenediamine were added to 25 cc. of methyl alcohol, in which had been dissolved 0.3 g. of metallic sodium, a slight excess over two molecular proportions. After boiling on the water bath for 45 minutes the solution was cooled and 4 g. of methyl oxide (4 mols) added. The mixture was allowed to stand for a half hour and found to be alkaline; it was then heated to the boiling temperature and digested for an hour or until neutral. Upon cooling the methylated product separated in the form of colorless, prismatic crystals. The yield was 0.7 g. The mother liquor was evaporated to dryness and the residue digested with water until the excess of iodide and alcohol was expelled. An insoluble precipitate was obtained which proved to be the methyl derivative. The total yield of this product was almost theoretical. Sodium iodide was found in the water filtrates in theoretical quantity.

If the original amide was treated with one molecular proportion of sodium instead of two, the methylation was only partially complete and a mixture resulted, from which it was difficult to separate the methylated from the unmethylated amide. Methyl alcohol, as a solvent, gave better results than ethyl alcohol, as in the latter methylation seemed to be incomplete and mixtures resulted from which pure substances could not be isolated. From the analysis of a product obtained under such conditions, it appeared that ethyl groups had replaced the phthalyl group. It was our experience that better yields of the methylated product were obtained when 2 g. portions were alkylated than when larger quantities were taken.

This ethylenediamine derivative crystallized in slender prisms. It is soluble in acetic acid and difficultly soluble in methyl alcohol. It melts at 177–178° to a clear oil. A mixture of this compound and the unmethylated derivative melted at 150–165°.

Calc. for $C_{13}H_{13}O_4N_2S$: N, 7.82, S, 8.9. Found: N, 7.94, 7.84, 7.97; S, 8.99.

Mono-Methylethylenediamine Hydrochloride, $CH_3NH.CH_2CH_2NH_2$. $2HCl.H_2O$.—In order to obtain this salt phthalimidobenzylsulfonmethyl

ethylenediamine was hydrolyzed by heating with an excess of concentrated hydrochloric acid at 120° for 4 hours. At the end of this time benzylchloride had formed a dark layer on the surface of the acid solution and phthalic acid had deposited in a crystalline condition. The contents of the bomb tube were diluted with water, filtered through a wet fluted filter and evaporated to dryness. The colorless residue left behind was triturated with a small amount of cold water and the insoluble phthalic acid filtered off. The aqueous solution of the amine hydrochloride was then evaporated to dryness and the hydrochloride dissolved in boiling 98% alcohol. On cooling, it separated in the form of colorless, micaeous flakes. After recrystallization from 98% alcohol it was then dried for analysis in a vacuum desiccator over concentrated sulfuric acid and potassium hydroxide. When dry hydrochloric acid gas was passed into the alcohol solution the hydrochloride separated very quickly. The amine distills with steam slowly. The hydrochloride melted at 130–132° with effervescence and the yield was practically theoretical.

Calc. for $C_6H_{10}N_2 \cdot 2HCl \cdot H_2O$: N, 16.98%. Found: N, 17.00, 17.20.

This base is not precipitated from an aqueous solution of its hydrochloride by mercuric chloride. Platinum chloride solution precipitates it from concentrated solutions in the form of square tabular prisms or plates, which melt at 240–242° with decomposition. The picrate of the base crystallizes from water in the form of prisms. They turn brown when heated and decompose at 220–222° with effervescence.

Dibenzylsulfonethylenediamine, $C_6H_5CH_2SO_2NHCH_2CH_2NHSO_2CH_2C_6H_5$.—This amide was prepared by heating the potassium salt of benzylsulfonamide with ethylenebromide at 130° for 5 hours. At 110° a vigorous reaction took place and it was necessary to cool the flask in order to retard the reaction. After the change was complete the reaction product was triturated with ether and the insoluble material washed with water to dissolve potassium bromide. The amide was then purified by crystallization from glacial acetic acid. It melted at 202–204°. The yield was 30% of theory. From the ether extract the unaltered dibromide and benzylsulfonamide were recovered. This amide crystallizes in the form of plates.

Calc. for $C_{16}H_{20}O_4N_2S_2$: N, 7.60%. Found: N, 7.63, 7.50.

Attempts to improve this yield were unsuccessful. In one experiment 3.6 g. of potassium hydroxide were dissolved in 50 cc. of absolute alcohol 10 g. of benzylsulfonamide were added and the mixture boiled until all the amide dissolved. One-half a molecular proportion of ethylenedibromide (5.4 g.) and 9.5 g. of potassium iodide were added and the solution digested until neutral. On cooling, the amide deposited mixed with potassium iodide and bromide. After washing with water the amide was purified by crystallization from alcohol. It melted at 202–204°. The yield

was very small. When ethylenebromide was used in excess the yield was not improved and unaltered amide was always recovered.

This same dibenzylsulfonamide can also be prepared by application of the Schotten and Baumann reaction with ethylenediamine and benzylsulfonchloride. From 5 g. of the amine and 15 g. of the sulfonchloride we obtained 4.5 g. of the purified amide melting at 204°. Two and five-tenths grams of acid chloride were recovered and the remainder was decomposed by the alkali.

The Alkylation of Dibenzylsulfonethylenediamine with Methyl Iodide. The Formation of Dibenzylsulfonmethylethylenediamine, $C_6H_5CH_2SO_2 \cdot N(CH_3)CH_2CH_2NH \cdot SO_2CH_2C_6H_5$, and Dibenzylsulfondimethylethylenediamine, $C_6H_5CH_2 \cdot SO_2 \cdot N(CH_3)CH_2CH_2N(CH_3) \cdot SO_2 \cdot CH_2C_6H_5$.—Ten grams of dibenzylsulfonethylenediamine and 2 molecular proportions of potassium hydroxide were dissolved in 150 cc. of 95% alcohol and the solution boiled for one hour. Six grams of methyl iodide were then added and the heating continued until the solution failed to respond to an alkaline reaction. After cooling, the insoluble material was separated and the filtrate saved (see below). This material was washed with cold water to remove potassium iodide and then triturated with a cold 10% solution of sodium hydroxide to remove any monomethylated amide and the insoluble material crystallized from glacial acetic acid. Four grams of material were obtained melting at 217–219°.

Calc. for $C_{18}H_{24}O_4N_2S_2$: N, 7.07%. Found: N, 7.08, 6.96.

From the alcohol filtrate and the sodium hydroxide washings (after acidifying) 1.5 g. of material were obtained. This product was partly soluble in cold alkali and alcohol. After treatment with alkali and reprecipitating with acid the amide was finally obtained pure and melted at 137°. The yield, however, was so small that there was not enough material for hydrolysis.

Calc. for $C_{17}H_{22}O_4N_2S_2$: N, 7.33%. Found: N, 7.33, 7.35.

Dimethylethylenediamine Hydrochloride, $CH_3NHCH_2CH_2NHCH_3 \cdot 2HCl$.—This salt was obtained by hydrolysis of dibenzylsulfondimethylethylenediamine with concentrated hydrochloric acid at 120–130°. The contents of the bomb tube were diluted with water, the solution filtered and finally evaporated to dryness. The amine hydrochloride was obtained in a crystalline condition and agreed in melting point and solubility with the dimethylethylenediamine hydrochloride described by Schneider.¹

Phthalimidophenylsulfonethylenediamine, $C_6H_4 \begin{array}{c} \diagup CO \\ \diagdown CO \end{array} N \cdot CH_2CH_2 \cdot$

$NHSO_2C_6H_5$.—This was obtained by heating 2.2 g. of bromoethylphthal-

¹ *Loc. cit.*

imide with 1.7 g. of the potassium salt of phenylsulfonamide for 4 hours at 100°. After washing with water to remove potassium bromide the amide was decolorized by digesting in 50% acetic acid with animal charcoal and then recrystallized from this same solvent. It crystallized in short, flat prisms which melted at 175°.

Calc. for $C_{16}H_{14}O_4N_2S$: N, 8.50%. Found: N, 8.8.

Di-(*p*-nitrobenzyl)-benzylsulfonamide, $C_6H_5CH_2SO_2N(CH_2.C_6H_4NO_2)_2$.—This amide and its corresponding *mono*-nitrobenzyl derivative were formed by alkylation of benzylsulfonamide with *p*-nitrobenzylchloride. They were separated by trituration with dilute sodium hydroxide solution (10%). The disubstituted derivative was insoluble and was purified by crystallization from glacial acetic acid. It separated in needles and melted at 193–194°.

Calc. for $C_{21}H_{19}O_6N_3S$: N, 9.52%. Found: N, 9.40, 9.39.

Acids precipitated from the alkaline washings the *mono*-nitrobenzylbenzylsulfonamide, $C_6H_5CH_2SO_2NHCH_2C_6H_4NO_2$. This was purified by crystallization from glacial acetic acid and melted at 182–183°. The yield was small.

Calc. for $C_{14}H_{14}O_4N_2S$: N, 9.15%. Found: N, 9.20.

Di-(*o*-nitrobenzyl)-benzylsulfonamide, $C_6H_5CH_2SO_2N(CH_2.C_6H_4NO_2)_2$.—This crystallized from glacial acetic acid in prisms, which melted at 169–170°.

Calc. for $C_{21}H_{19}O_6N_3S$: N, 9.52%. Found: N, 9.35, 9.32.

***o*-Nitrobenzylbenzylsulfonamide**, $C_6H_5CH_2SO_2NHCH_2C_6H_4NO_2$.—This crystallizes from alcohol and melts at 124–126°. It is soluble in 10% sodium hydroxide solution.

Calc. for $C_{14}H_{14}O_4N_2S$: N, 9.15%. Found: N, 9.0, 8.9.

Preparation of Di-(*o*-nitrobenzyl)amine Hydrochloride, $(NO_2.C_6H_4CH_2)_2NH.HCl$.—This was easily obtained by heating its corresponding sulfonamide (see above) with concentrated hydrochloric acid at 130–140°. It melted at 245° after crystallization from water. Gabriel and Jansen¹ have described this salt and assigned to it a melting point of 220°.

Calc. for $C_{14}H_{13}O_4N_3.HCl$: N, 12.9%. Found: N, 12.3, 12.4.

Di-(*p*-nitrobenzyl)amine Hydrochloride, $(NO_2C_6H_4CH_2)_2NH.HCl$.—This was obtained by hydrolysis of its sulfonamide with strong hydrochloric acid. It crystallized from water and melted at 212°. Strakosch² has described this salt and assigned to it a melting point of 212°.

Calc. for $C_{14}H_{13}O_4N_3.HCl$: N, 12.9%. Found: N, 12.9.

¹ *Ber.*, 24, 3093 (1891).

² *Ibid.*, 6, 1056 (1873).

Benzylsulfonaminopropionamide, (XVII).—The α -bromopropionbromide used in this experiment was prepared according to the directions of Zelinsky¹ and converted into the corresponding α -bromopropionamide by the method described by Bischoff.² Twenty-eight and two-tenths grams of benzylsulfonamide were converted into its potassium salt and the latter digested in alcohol with 25 g. of α -bromopropionamide for 6 hours. The liquor was still alkaline at the end of this time due to the presence of ammonia formed by hydrolysis. On cooling the propionamide deposited mixed with potassium bromide. This was washed with water and purified by recrystallization from hot water. It crystallized in prisms and melted at 167°. The compound is soluble in alcohol, water and acetic acid, and difficultly soluble in benzene and ether. The yield was 15 g.

Calc. for $C_{10}H_{14}O_3N_2S$: N, 11.57%. Found: N, 11.6, 11.56.

Benzylsulfonalanine, (XVIII).—The amide described above was hydrolyzed by boiling with a strong aqueous solution of barium hydroxide or until no ammonia was evolved. The barium was then exactly precipitated as barium sulfate and the filtrate evaporated to dryness. The acid remained as a crystalline residue and was purified by crystallization from boiling water. It separated in the form of plates which melted at 164–165°. A mixture of this with the unaltered amide melted at 155°.

Calc. for $C_{10}H_{13}O_4NS$: N, 5.75; S, 13.16. Found: N, 6.0, 5.8; S, 13.6.

Hydrolysis of Benzylsulfonalanine with Hydrochloric Acid. Alanine Hydrochloride, (XIX).—This change was accomplished by heating the sulfonamide with hydrochloric acid for 2 hours at 130°. After filtering the solution was evaporated to dryness and the alanine hydrochloride purified by crystallization.³

Calc. for $C_3H_7O_2N.HCl$: N, 11.2%. Found: N, 11.3.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

ON THE REACTION OF BOTH THE IONS AND THE NONIONIZED FORMS OF ACIDS, BASES AND SALTS: THE REACTION OF METHYL IODIDE WITH SODIUM, POTASSIUM AND LITHIUM ETHYLATES AT 0°.⁴

[TWENTY-FOURTH COMMUNICATION ON CATALYSIS.]

BY BESSIE M. BROWN AND S. F. ACREE.

Received July 28, 1916.

A theory concerning chemical reactions was brought out by Brunel⁵ and one of us in 1905–6, and Johnson⁶ in 1907, when they showed by ex-

¹ *Ber.*, 20, 2026 (1887).

² *Ibid.*, 30, 2312 (1897).

³ Strecker, *Ann.*, 75, 29 (1850).

⁴ We are indebted to the Carnegie Institution of Washington for aid in this work.

⁵ *Am. Chem. J.*, 43, 505 (1910).

⁶ *Ibid.*, 38, 259, 260 (1907).